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Rhodium Bis(quinoliny)benzene Complexes for Methane Activation and Functionalization

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DFT screening of Rh complexes

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We screened complexes of rhodium with the following ligands, as depicted in Figure S1:

- the bis(N-phenyl) benzylamidinate (NN) ligand and its fluorinated analogue (NN^F),
- the (N-phenyl) acetaldiminyl quinolate (ONN) ligand and its related (ONN^F) and (ONN^{NMe2}) ligands,
- the bis(pyridyl) methanesulfonate (DPMS) and bis(pyridyl) ethanesulfonate (DPES) ligands,
- the bis(pyrrolyl) quinoliny phosphine (PN) ligand.

For each of these ligands complexed with rhodium, we generated catalytic cycles in the template of Scheme 1. For the (DPMS), (DPES), (PN), and (ONN^x) family of ligands, we found that both the methane activation energy and the methyl functionalization energy were too high for effective catalysis (Table S1). However, we found lower numbers for the (NN^x) family of ligands.

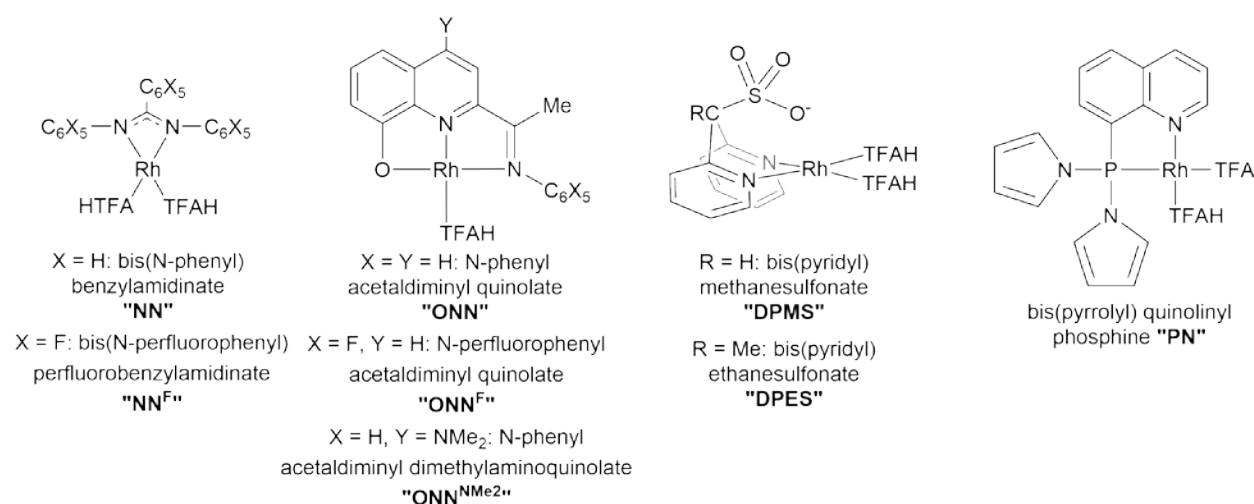


Figure S1. The rhodium complexes screened. For each complex, the Rh^I form in TFAH is shown here, but full catalytic cycles were computed. The best kinetics were predicted for the Rh(NN) and Rh(NN^F) complexes.

TS type		Rh(NN)	Rh(NN ^F)	Rh(ONN)	Rh(ONN ^F)
Act.	Rh ^{III} + CH ₄ ^{ax}	32.6/34.8	27.6/29.6	37.2/39.8	35.8/37.8
	Rh ^{III} + CH ₄ ^{eq}	38.3/40.4	33.7/36.3	37.9/40.7	38.1/40.1
Func.	Rh ^{III-I} + TFA	54.8/60.3	42.7/48.2	44.2/49.3	41.7/45.8
	Rh ^{III-II} + VOCl ₃	43.2/44.2	38.1/40.0	40.4/42.5	39.1/40.8
	Rh ^{III-IV-II} + TFA	42.2/48.6	36.8/43.6	N/A	N/A
TS type		Rh(ONN ^{NMe2})	Rh(DPMS)	Rh(DPES)	Rh(PN)

Act.	Rh^{III} + CH₄^{ax}	38.7/41.2	38.0/40.2	41.0/44.0	40.1/43.0
	Rh^{III} + CH₄^{eq}	40.0/42.9	33.9/36.2	35.6/38.4	35.0/37.7
Func.	Rh^{III-I} + TFA	46.7/52.6	46.6/51.3	53.8/59.3	38.3/43.8
	Rh^{III-II} + VOCl₃	41.4/43.4	41.0/41.6	45.5/47.4	47.7/56.9
	Rh^{III-IV-II} + TFA	N/A	49.3/56.3	49.9/57.1	N/A

Table S1. Lowest activation and functionalization energies for each series of Rh-ligand complexes in TFAH. For each entry, the first number is at 298 K and the second at 498 K. Not all III-IV-II transition states were calculated. All free energies in kcal/mol.

Rh^{III-I} S_N2 and Rh^{III-II} S_R2 methyl functionalization pathways

Figure S2 shows the functionalization transition states for S_N2 attack by TFA[−]/TFAH on various Rh–Me intermediates. Both H⁺ pre-protonation followed by TFA[−] attack and concerted TFAH attack/deprotonation transition states were investigated. The lowest energy S_N2 functionalization barrier was found to arise from the attack of a TFA[−] ion on a protonated Rh–Me_{ax} species. Not surprisingly, lower barriers were found for Rh^{III}(bisq^x) complexes with less electron-donating ligands. For example, Rh^{III}(bisq^{Me4}) complexes have a minimum barrier of 36.2 kcal/mol at 298 K, but this decreases to 31.8 kcal/mol at 298 K for unsubstituted Rh^{III}(bisq) complexes, and decreases further to 29.9 kcal/mol at 298 K for Rh^{III}(bisq^{F4}) complexes. The energies are overall significantly lower than those found with other ligand families, thus confirming our initial hypothesis that a weak η²-benzene coordinated *trans* to the methyl will facilitate S_N2 attack. Indeed, barriers of 34.1 kcal/mol and lower at 298 K are found for (bisq) and its fluorinated analogues, thereby establishing the viability of the Rh^{III}(bisq^x) family of complexes as potentially effective catalysts.

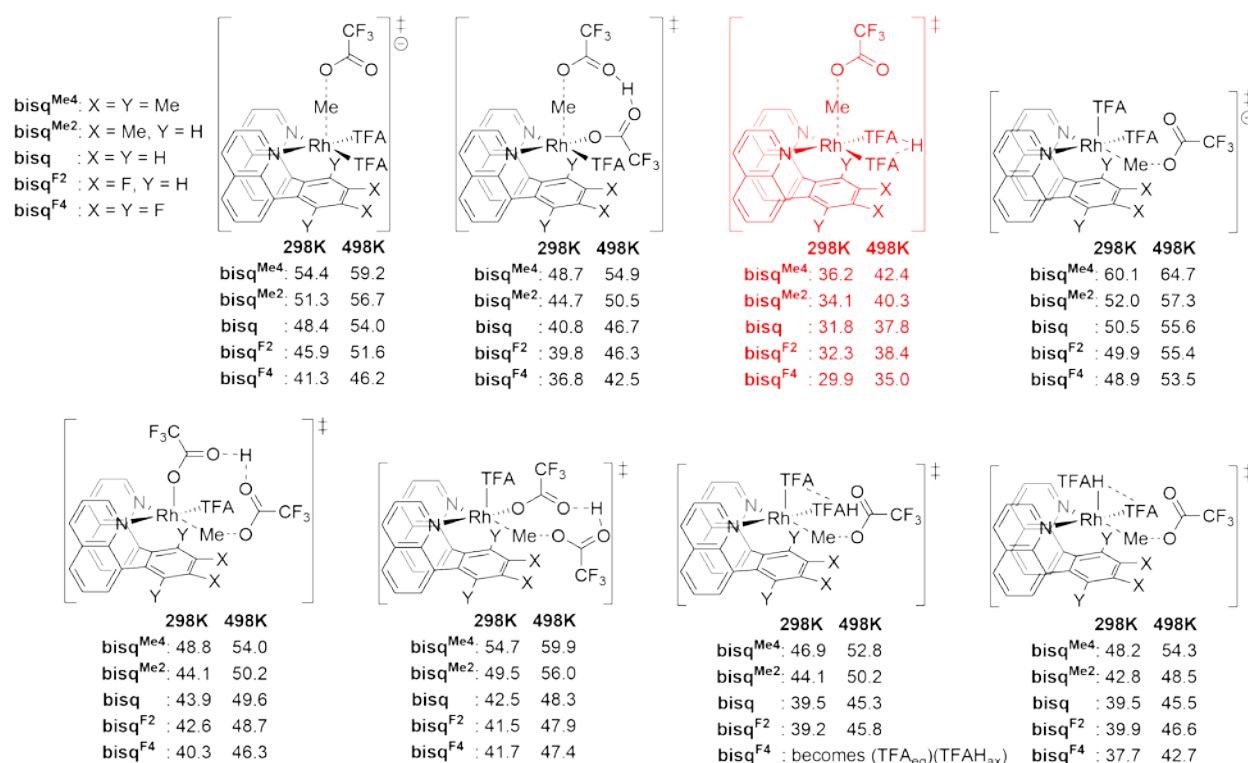


Figure S2. The various $\text{Rh}^{\text{III}}(\text{bisq}^{\text{x}})(\text{Me})$ functionalization transition states for the III-I $\text{S}_{\text{N}}2$ pathway. All transition states resulting from TFA^-/TFAH attack on each $\text{Rh}-\text{Me}$ species, axial and equatorial, neutral and positively charged, are shown. The lowest transition state for each (bisq^{x}) ligand is shown in red. All free energies are in kcal/mol and referenced to the corresponding $\text{Rh}^{\text{III}}(\text{bisq}^{\text{x}})(\text{TFA})_3$ species.

Figure S3 shows the functionalization transition states for $\text{S}_{\text{R}}2$ attack by OVCl_3 on both neutral $\text{Rh}^{\text{III}}(\text{bisq}^{\text{x}})(\text{Me})(\text{TFA})_2$ and protonated $[\text{Rh}^{\text{III}}(\text{bisq}^{\text{x}})(\text{Me})(\text{TFA})(\text{TFAH})]^+$ species, with both axial and equatorial methyl conformations. In most cases, the lowest energy $\text{S}_{\text{R}}2$ functionalization barrier was found to arise from the attack of an OVCl_3 molecule on a neutral $\text{Rh}-\text{Me}_{\text{ax}}$ species (the exception is $(\text{bisq}^{\text{Me4}})$, which prefers a protonated transition state). As in the III-I $\text{S}_{\text{N}}2$ case, lower barriers were found for $\text{Rh}^{\text{III}}(\text{bisq}^{\text{x}})$ complexes with less electron-donating ligands, and overall the barriers were reduced compared to those of other ligand families; although the effect is not as pronounced as for the $\text{S}_{\text{N}}2$ case, and the tetrafluorinated $(\text{bisq}^{\text{F4}})$ version is an outlier.

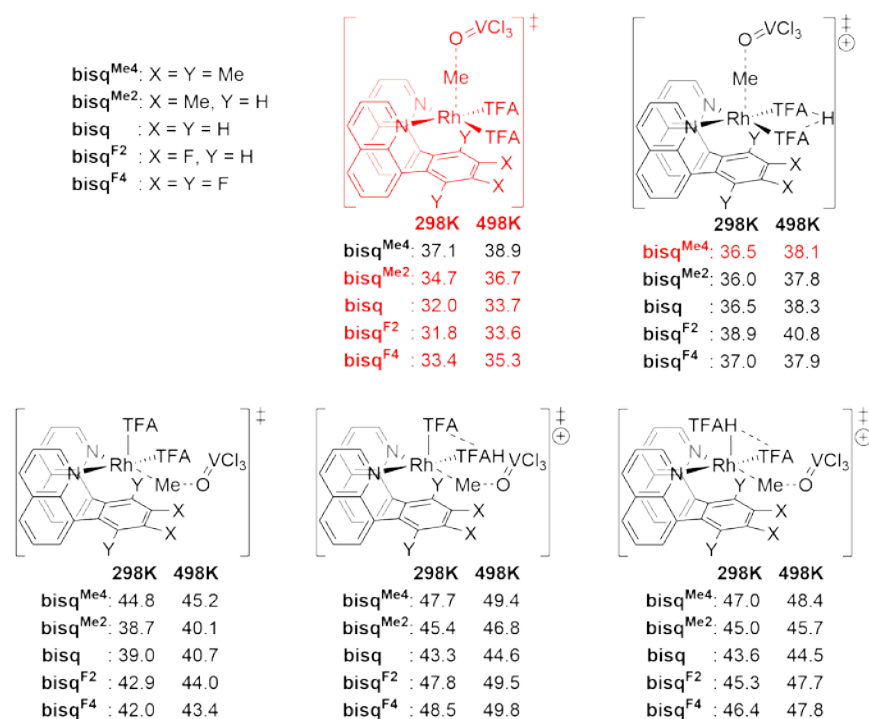
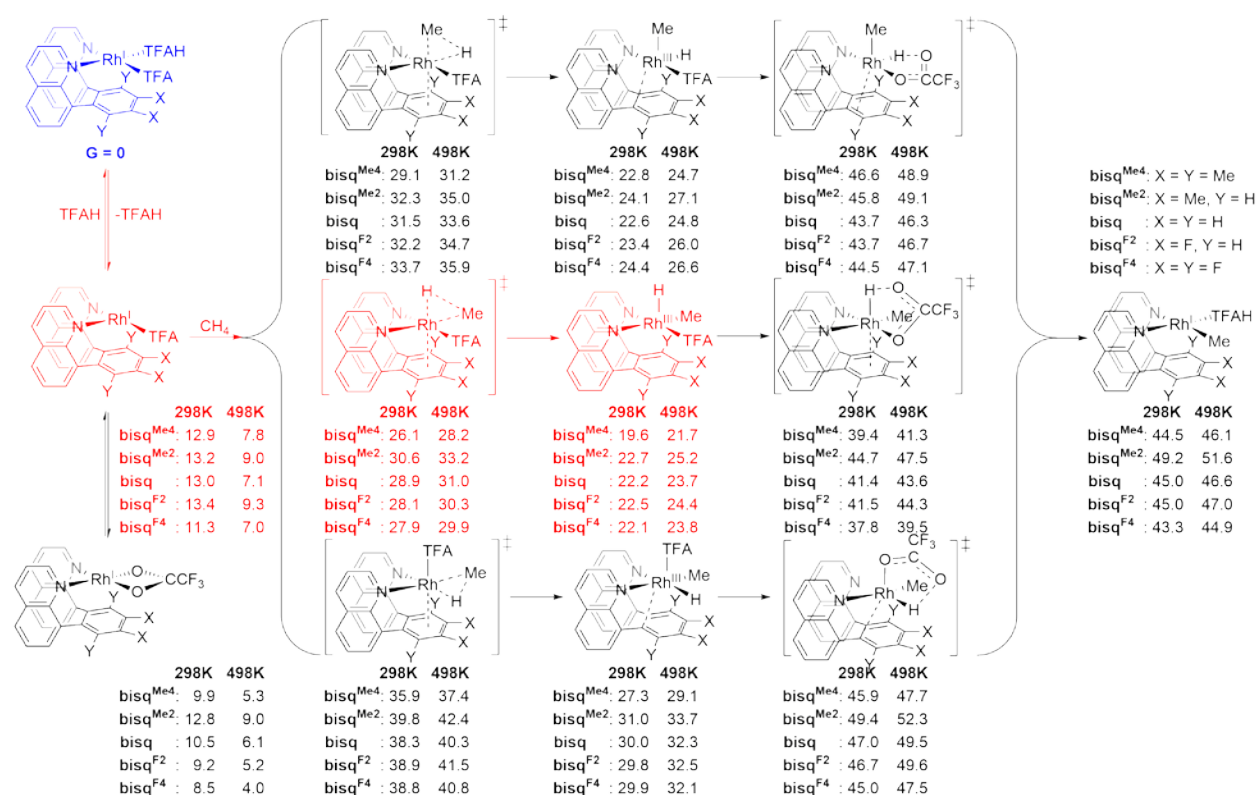


Figure S3. The various $\text{Rh}^{\text{III}}(\text{bisq}^{\text{x}})(\text{Me})$ functionalization transition states for the III-II $\text{S}_{\text{R}}2$ pathway. All transition states resulting from OVCl_3 attack on each $\text{Rh}-\text{Me}$ species, axial and equatorial, neutral and positively charged, are shown. The lowest transition state for each (bisq^{x}) ligand is shown in red. All free energies are in kcal/mol and referenced to the corresponding $\text{Rh}^{\text{III}}(\text{bisq}^{\text{x}})(\text{TFA})_3$ species.

Methane activation by oxidative addition

An alternative pathway, which we term I-III, involves the direct C-H oxidative addition by a Rh^{I} species to a Rh^{III} hydride methyl. However, given the oxidizing nature of the reaction conditions, we do not anticipate this to be a fruitful pathway, as any catalytic cycle involving a $\text{Rh}^{\text{I-III}}$ cycle would likely suffer from the fact that oxidation of the Rh^{I} species to Rh^{III} would act as a thermodynamic sink. Hence, this alternative option was not considered as viable in this investigation.



Scheme S1. Catalytic cycle for the activation and functionalization of methane using Rh(bisq^X) complexes in TFAH, *via* the Rh^{I-III} pathway. Blue denotes the resting state and red the most favored pathway. All free energies are in kcal/mol.

Tables of Cartesian coordinates and thermodynamic values

All Cartesian coordinates in Å.

Explanation for row entries

- Temp: temperature, in Kelvins
- E_{gas}: gas-phase electronic energies, in hartrees
- E_{solv}: solution-phase electronic energies, in hartrees
- G: free energy, as calculated in the Computational Details section, in hartrees
- ZPE: zero-point energy, in kcal/mol
- H_{vib}: vibrational enthalpy, in kcal/mol
- S_{trans}: translational entropy, in cal/mol K
- S_{rot}: rotational entropy, in cal/mol K
- S_{vib}: vibrational entropy, in cal/mol K
- Solv: solvation energy, equal to E_{solv} – E_{gas}, in kcal/mol
- H_{tot}: total enthalpy, in kcal/mol (for gases and pure liquids)
- S_{tot}: total entropy, in kcal/mol (for gases and pure liquids)
- ΔG_{gas→liquid}: free energy change from gas to liquid, as calculated in the Computational Details section, in kcal/mol (for pure liquids)

Rh(bisq) complexes

Table S2. Rh^I(bisq)(TFA)(TFAH) Cartesian coordinates

Atom	x	y	z
Rh1	-1.12725	0.431032	-1.50283

N2	-1.61698	-0.91991	-0.03009
C3	-1.77884	-2.18818	-0.40863
C4	-2.50143	-3.12986	0.348164
C5	-3.09845	-2.7268	1.519699
C6	-5.49088	2.592302	-1.54048
C7	-5.21957	1.363774	-2.0878
C8	-3.93614	0.817847	-1.9099
N9	-2.95864	1.416154	-1.22916
H10	-1.33372	-2.45206	-1.36084
H11	-2.60295	-4.14369	-0.02437
H12	-3.70819	-3.40935	2.105509
H13	-3.67809	-0.13607	-2.35409
O14	0.512798	-0.84374	-1.90562
C15	1.731422	-0.66829	-2.04344
O16	2.380504	0.408952	-2.25724
C17	2.644501	-1.90973	-1.94236
F18	3.394071	-2.0403	-3.0499
F19	3.471758	-1.78588	-0.88663
F20	1.930557	-3.03343	-1.78344
O21	-0.89836	1.828482	-3.08349
C22	0.091056	2.540356	-3.3613
O23	1.300629	2.418978	-3.03289
C24	-0.20897	3.81052	-4.1937
F25	-0.24199	4.883264	-3.36517
F26	0.739139	4.035539	-5.11725
F27	-1.39312	3.742646	-4.82019
H28	1.775943	1.312914	-2.52684
C29	-3.20855	2.635827	-0.63181
C30	-4.48997	3.262783	-0.79836
C31	-4.74386	4.5394	-0.23566
C32	-3.76559	5.186277	0.475536
C33	-2.51477	4.563794	0.662003
C34	-2.21083	3.312725	0.14396
H35	-5.7216	4.989149	-0.38527
H36	-3.94758	6.166999	0.904874
H37	-1.7539	5.07147	1.247141
C39	-2.0788	-0.52407	1.209859
C40	-2.89754	-1.40383	1.987246
C41	-3.4615	-0.94135	3.204149
C42	-3.18948	0.32795	3.654313

C43	-2.30031	1.156319	2.934542
C44	-1.7278	0.756553	1.738676
H45	-4.09835	-1.61296	3.773711
H46	-3.6199	0.685443	4.585174
H47	-2.02346	2.123206	3.34432
H49	-5.95685	0.814555	-2.66309
H50	-6.4607	3.06621	-1.66613
C51	-0.84701	2.784751	0.434824
C52	-0.62661	1.593378	1.158252
C53	0.686807	1.239089	1.50131
C54	1.773723	2.020367	1.112855
C55	1.557668	3.187671	0.384166
C56	0.256771	3.566	0.058674
H59	0.850708	0.335114	2.081438
H60	2.781884	1.716936	1.380354
H61	2.394717	3.799437	0.061406
H62	0.087591	4.461348	-0.53232

Table S3. Rh^I(bisq)(TFA)(TFAH) thermodynamic values

Temp	298.15	498.15
E_{gas}	-2195.68	-2195.68
E_{solv}	-2195.70	-2195.70
G	-2195.35	-2195.41
ZPE	251.644	251.644
H_{vib}	20.095	52.112
S_{trans}	45.352	47.902
S_{rot}	37.620	39.150
S_{vib}	131.918	212.651
solv	-13.3	-13.3

Table S4. Rh^I(bisq)(κ¹-TFA) Cartesian coordinates

Atom	x	y	z
Rh1	-1.44085	0.364556	-1.85191
N2	-2.19404	-1.00806	-0.44084
C3	-2.83659	-2.11484	-0.7919
C4	-3.62195	-2.86855	0.104396

C5	-3.74347	-2.43769	1.402932
C6	-5.54855	2.92677	-1.324
C7	-5.51925	1.737938	-2.01353
C8	-4.30299	1.03656	-2.11426
N9	-3.16285	1.464438	-1.57418
H10	-2.72672	-2.42213	-1.82556
H11	-4.11984	-3.76556	-0.24834
H12	-4.35736	-2.97613	2.120228
H13	-4.24189	0.096943	-2.65265
O14	0.226238	-0.61091	-2.45587
C15	0.829803	-1.57575	-1.85424
O16	0.547855	-2.15499	-0.81242
C17	2.120402	-1.98044	-2.61494
F18	2.653163	-3.11253	-2.12661
F19	1.894207	-2.17068	-3.93245
F20	3.058384	-1.00837	-2.50137
C21	-4.36097	3.416439	-0.72583
C22	-3.16445	2.643638	-0.85683
C23	-1.95138	3.103081	-0.26676
C24	-1.96755	4.317659	0.400814
C25	-3.14336	5.089622	0.52726
C26	-4.32325	4.645146	-0.01924
H27	-1.04361	4.676141	0.844891
H28	-3.10789	6.033783	1.06282
H29	-5.2373	5.225442	0.072151
C30	-3.0449	-1.27909	1.825515
C31	-2.23103	-0.58819	0.871358
C32	-1.4461	0.5309	1.30053
C33	-1.55589	0.946127	2.61668
C34	-2.40459	0.300794	3.543162
C35	-3.12586	-0.80275	3.158952
H36	-0.94971	1.784325	2.947338
H37	-2.46212	0.668292	4.563605
H38	-3.75938	-1.33217	3.86591
H39	-6.40772	1.329538	-2.48311
H40	-6.46649	3.500499	-1.2297
C41	-0.65839	2.349907	-0.35263
C42	-0.40847	1.183194	0.430447
C43	0.909222	0.713395	0.54496
C44	1.957551	1.326422	-0.14106

C45	1.714373	2.449252	-0.92879
C46	0.421803	2.966119	-1.01649
H47	1.095021	-0.17418	1.139469
H48	2.9611	0.919564	-0.06211
H49	2.526059	2.930262	-1.46658
H50	0.230953	3.864885	-1.59664

Table S5. Rh^I(bisq)(κ^1 -TFA) thermodynamic values

Temp	298.15	498.15
E_{gas}	-1668.87	-1668.87
E_{solv}	-1668.90	-1668.90
G	-1668.58	-1668.63
ZPE	227.181	227.181
H_{vib}	14.496	39.918
S_{trans}	44.789	47.339
S_{rot}	36.546	38.077
S_{vib}	101.556	167.588
solv	-17.8	-17.8

Table S6. Rh^I(bisq)(κ^2 -TFA) Cartesian coordinates

Atom	x	y	z
Rh1	-1.31046	0.49712	-1.93378
N2	-1.89723	-0.85885	-0.50869
C3	-2.38347	-2.02805	-0.92695
C4	-3.10517	-2.90667	-0.09658
C5	-3.34799	-2.54391	1.207037
C6	-5.45239	3.009708	-1.33894
C7	-5.35649	1.845355	-2.05944
C8	-4.1154	1.187027	-2.11652
N9	-3.0128	1.620335	-1.50308
H10	-2.20945	-2.25965	-1.97162
H11	-3.47726	-3.839	-0.50802
H12	-3.93326	-3.17623	1.869085
H13	-3.99811	0.278445	-2.69486
O14	-0.38366	1.540437	-3.62015
C15	0.458218	0.601444	-3.66499

O16	0.416403	-0.3848	-2.8739
C17	1.542351	0.627274	-4.75371
F18	2.6531	-0.01587	-4.35788
F19	1.087046	0.017618	-5.87098
F20	1.878915	1.886102	-5.08007
C21	-4.31163	3.509486	-0.66635
C22	-3.07923	2.777735	-0.74913
C23	-1.92863	3.287286	-0.06319
C24	-2.05018	4.482062	0.631001
C25	-3.25961	5.203393	0.70294
C26	-4.37661	4.720036	0.069794
H27	-1.17323	4.865293	1.144183
H28	-3.29861	6.132948	1.263181
H29	-5.32265	5.252899	0.11286
C30	-2.81126	-1.33036	1.70534
C31	-2.031	-0.51536	0.823382
C32	-1.37477	0.645008	1.337145
C33	-1.59833	0.99877	2.657751
C34	-2.43217	0.240398	3.508263
C35	-3.01178	-0.9169	3.047318
H36	-1.08905	1.872744	3.052854
H37	-2.58306	0.560162	4.535238
H38	-3.62077	-1.53677	3.69993
H39	-6.20452	1.427968	-2.59155
H40	-6.38672	3.561001	-1.27584
C41	-0.58242	2.642372	-0.06415
C42	-0.33215	1.401336	0.566004
C43	0.988155	0.933281	0.64577
C44	2.042273	1.642494	0.072905
C45	1.793992	2.85814	-0.56049
C46	0.492759	3.356965	-0.61064
H47	1.180845	-0.00725	1.153826
H48	3.05267	1.247704	0.129921
H49	2.607242	3.422293	-1.00793
H50	0.294297	4.302922	-1.10578

Table S7. Rh^I(bisq)(κ²-TFA) thermodynamic values

Temp	298.15	498.15
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E_{gas}	-1668.88	-1668.88
E_{solv}	-1668.91	-1668.91
G	-1668.58	-1668.64
ZPE	227.713	227.713
H_{vib}	15.353	41.502
S_{trans}	44.789	47.339
S_{rot}	36.618	38.148
S_{vib}	97.996	163.852
solv	-14.1	-14.1

Table S8. Rh^I(bisq)(Me) Cartesian coordinates

Atom	x	y	z
Rh1	-1.08591	0.8459	-1.84684
N2	-2.32654	-0.2764	-0.38103
C3	-3.37825	-1.02152	-0.69242
C4	-4.07826	-1.80462	0.249543
C5	-3.65558	-1.80787	1.55871
C6	-5.53028	2.960911	-2.05833
C7	-5.15494	2.302872	-3.20496
C8	-3.83158	1.817695	-3.3117
N9	-2.91731	1.976299	-2.3652
H10	-3.68614	-0.9994	-1.73444
H11	-4.93269	-2.39169	-0.0716
H12	-4.1641	-2.40545	2.311023
H13	-3.51072	1.280976	-4.20014
C22	-4.58288	3.161413	-1.02037
C23	-3.2555	2.674411	-1.22005
C24	-2.26137	2.875356	-0.2098
C25	-2.63478	3.50821	0.962715
C26	-3.9585	3.957605	1.178908
C27	-4.91335	3.802776	0.201963
H28	-1.88361	3.671989	1.729899
H29	-4.21139	4.4421	2.117937
H30	-5.92931	4.159724	0.350979
C31	-2.53555	-1.02412	1.935206
C32	-1.89711	-0.24696	0.921387
C33	-0.76529	0.564178	1.227013
C34	-0.29304	0.544295	2.531833
C35	-0.90878	-0.23421	3.538082

C36	-2.01641	-0.99927	3.254838
H37	0.565241	1.159095	2.785419
H38	-0.5036	-0.21559	4.546058
H39	-2.4983	-1.59631	4.024605
H40	-5.85242	2.140886	-4.02072
H41	-6.54452	3.32942	-1.9289
C42	-0.81885	2.505569	-0.47768
C43	-0.10389	1.41408	0.189415
C44	1.323775	1.443527	0.1897
C45	2.040792	2.486603	-0.36057
C46	1.352832	3.59016	-0.91238
C47	-0.02203	3.606643	-0.95749
H48	1.84473	0.613508	0.660688
H49	3.126623	2.467256	-0.34929
H50	1.91233	4.437185	-1.30149
H51	-0.54236	4.464544	-1.37425
C52	0.112655	1.561219	-3.33845
H53	1.115222	1.820486	-2.97869
H54	0.185096	0.714196	-4.04576
H55	-0.30002	2.424891	-3.87487

Table S9. Rh^I(bisq)(Me) thermodynamic values

Temp	298.15	498.15
E_{gas}	-1182.55	-1182.55
E_{solv}	-1182.57	-1182.57
G	-1182.23	-1182.28
ZPE	231.164	231.164
H_{vib}	12.363	35.124
S_{trans}	44.202	46.752
S_{rot}	35.253	36.783
S_{vib}	76.125	133.368
solv	-9.4	-9.4

Table S10. Rh^I(bisq)(Me)(TFAH) Cartesian coordinates

Atom	x	y	z
Rh1	-1.28269	0.631026	-2.24416

N2	-2.17774	-0.2698	-0.31143
C3	-3.12905	-1.12303	-0.67331
C4	-3.81376	-1.97473	0.21657
C5	-3.47443	-1.93787	1.545317
C6	-5.33957	3.137736	-2.0096
C7	-4.89447	2.552085	-3.16941
C8	-3.57995	2.052562	-3.22657
N9	-2.71489	2.115243	-2.20634
H10	-3.35504	-1.14416	-1.73549
H11	-4.57938	-2.64373	-0.16213
H12	-3.96082	-2.58367	2.272046
H13	-3.21808	1.56149	-4.11935
O14	-0.13044	-1.18056	-2.4203
C15	1.088888	-1.04425	-2.44775
O16	1.722045	0.092092	-2.31294
C17	2.024073	-2.24215	-2.65228
F18	2.703802	-2.10497	-3.80353
F19	2.911875	-2.3182	-1.64463
F20	1.331345	-3.38304	-2.69694
H21	0.986627	0.784154	-2.2187
C22	-4.44705	3.271133	-0.91619
C23	-3.10672	2.783084	-1.05779
C24	-2.1823	2.988823	0.010018
C25	-2.6306	3.585799	1.178337
C26	-3.9647	4.01393	1.338443
C27	-4.85384	3.874998	0.300502
H28	-1.921	3.747272	1.98388
H29	-4.27375	4.473853	2.272687
H30	-5.87885	4.225488	0.390503
C31	-2.46562	-1.04645	1.985067
C32	-1.83173	-0.19266	1.018409
C33	-0.81626	0.715907	1.474034
C34	-0.4716	0.701081	2.818686
C35	-1.08924	-0.14955	3.758324
C36	-2.07994	-1.00567	3.348859
H37	0.295363	1.391211	3.157724
H38	-0.78289	-0.11265	4.799684
H39	-2.57994	-1.66538	4.053184
H40	-5.5362	2.446787	-4.0382
H41	-6.35628	3.509282	-1.91426

C42	-0.71515	2.713195	-0.11034
C43	-0.07607	1.678449	0.606385
C44	1.327372	1.614928	0.597525
C45	2.095592	2.541777	-0.10593
C46	1.460525	3.5681	-0.80534
C47	0.070188	3.653397	-0.79444
H48	1.817305	0.812081	1.141275
H49	3.178651	2.461956	-0.10408
H50	2.043442	4.305814	-1.34968
H51	-0.42642	4.46155	-1.32333
C52	-0.52269	1.277137	-4.06032
H53	0.27518	2.029357	-3.95434
H54	-0.11312	0.44107	-4.64705
H55	-1.30129	1.748444	-4.67721

Table S11. Rh^I(bisq)(Me)(TFAH) thermodynamic values

Temp	298.15	498.15
E_{gas}	-1709.34	-1709.34
E_{solv}	-1709.36	-1709.36
G	-1708.99	-1709.05
ZPE	257.030	257.030
H_{vib}	17.175	45.777
S_{trans}	44.875	47.425
S_{rot}	36.784	38.314
S_{vib}	111.273	183.332
solv	-10.1	-10.1

Table S12. Rh^{II}(bisq)(TFA)₂ Cartesian coordinates

Atom	x	y	z
Rh1	-0.82986	0.747443	-1.84171
N2	-1.64756	-0.71621	-0.56335
C3	-2.11461	-1.84007	-1.09777
C4	-2.92121	-2.74553	-0.37723
C5	-3.25963	-2.4528	0.921314
C6	-5.21477	2.938823	-1.83323
C7	-4.91024	1.879785	-2.65236

C8	-3.61854	1.322778	-2.58968
N9	-2.67851	1.761366	-1.75814
H10	-1.81683	-2.02523	-2.12613
H11	-3.26974	-3.64748	-0.8684
H12	-3.9003	-3.11462	1.497767
H13	-3.32199	0.523269	-3.25919
O14	0.985403	-0.22057	-2.0039
C15	0.974436	-1.2855	-2.72323
O16	0.018349	-1.85352	-3.24724
C17	2.397899	-1.87502	-2.89418
F18	2.929306	-2.18895	-1.68924
F19	2.387775	-2.99145	-3.63663
F20	3.223666	-0.98974	-3.48638
O21	-0.11417	2.168678	-3.17737
C22	-0.59065	1.885173	-4.33439
O23	-1.37439	0.97476	-4.61373
C24	-0.10603	2.851958	-5.44036
F25	-0.5671	4.102105	-5.19867
F26	1.237946	2.913955	-5.48437
F27	-0.54555	2.482458	-6.65136
C29	-4.23244	3.45022	-0.95038
C30	-2.94464	2.823768	-0.9238
C31	-1.93537	3.338371	-0.05257
C32	-2.23592	4.446673	0.722258
C33	-3.505	5.063749	0.698618
C34	-4.49084	4.56962	-0.11949
H35	-1.46256	4.847082	1.371279
H36	-3.69233	5.927929	1.32872
H37	-5.47387	5.030944	-0.15504
C38	-2.75707	-1.27573	1.530877
C39	-1.909	-0.42476	0.756428
C40	-1.32111	0.725187	1.360496
C41	-1.6421	1.017949	2.674587
C42	-2.52051	0.208485	3.428021
C43	-3.05796	-0.92767	2.871946
H44	-1.18385	1.884402	3.142381
H45	-2.74674	0.477656	4.455409
H46	-3.71043	-1.57775	3.448387
H47	-5.62991	1.472103	-3.35354
H48	-6.19618	3.404958	-1.85801

C49	-0.55149	2.779098	0.032939
C50	-0.27019	1.542651	0.66799
C51	1.072907	1.152011	0.832956
C52	2.11474	1.946316	0.373163
C53	1.836072	3.165183	-0.24856
C54	0.518951	3.57704	-0.40934
H55	1.285518	0.207113	1.323336
H56	3.140631	1.612318	0.493182
H57	2.644531	3.78843	-0.61834
H58	0.298751	4.515269	-0.90804

Table S13. Rh^{II}(bisq)(TFA)₂ thermodynamic values

Temp	298.15	498.15
E_{gas}	-2195.07	-2195.07
E_{solv}	-2195.11	-2195.11
G	-2194.76	-2194.83
ZPE	246.414	246.414
H_{vib}	19.401	50.676
S_{trans}	45.348	47.898
S_{rot}	37.562	39.092
S_{vib}	131.022	210.900
solv	-20.5	-20.5

Table S14. [Rh^{II}(bisq)(TFA)(TFAH)]⁺ Cartesian coordinates

Atom	x	y	z
Rh1	-1.13473	0.560841	-1.434
N2	-1.80134	-0.86917	-0.08975
C3	-2.10189	-2.08605	-0.5304
C4	-2.77942	-3.0326	0.26006
C5	-3.1751	-2.67508	1.529268
C6	-5.55169	2.564563	-1.62533
C7	-5.21622	1.412141	-2.29626
C8	-3.91794	0.901737	-2.13937
N9	-2.99606	1.470456	-1.3664
H10	-1.80504	-2.318	-1.54874
H11	-2.99433	-4.0126	-0.15052

H12	-3.73056	-3.3683	2.154105
H13	-3.61659	0.003249	-2.66947
O14	0.530593	-0.73184	-1.6623
C15	1.763738	-0.65258	-1.81227
O16	2.471442	0.364347	-2.09872
C17	2.574029	-1.96411	-1.67085
F18	3.743196	-1.73246	-1.06821
F19	1.88749	-2.86372	-0.95515
F20	2.800339	-2.46641	-2.89353
O21	-0.79513	1.929407	-2.96733
C22	0.247313	2.55628	-3.31543
O23	1.436083	2.368093	-2.99084
C24	-0.04202	3.77925	-4.22248
F25	-0.48673	4.786661	-3.43395
F26	1.050708	4.193458	-4.8611
F27	-0.99429	3.500746	-5.12194
H28	1.922358	1.251015	-2.41749
C29	-3.29191	2.625956	-0.67735
C30	-4.59623	3.206457	-0.80273
C31	-4.89595	4.417243	-0.12706
C32	-3.93634	5.040965	0.631642
C33	-2.65167	4.469252	0.748276
C34	-2.31096	3.277668	0.127393
H35	-5.88911	4.84317	-0.2336
H36	-4.15533	5.973242	1.142216
H37	-1.90151	4.973385	1.350389
C38	-2.09898	-0.50966	1.203513
C39	-2.84495	-1.39538	2.040075
C40	-3.20564	-0.97067	3.345118
C41	-2.81491	0.267699	3.798648
C42	-2.01455	1.105746	2.988095
C43	-1.64122	0.738798	1.70694
H44	-3.78021	-1.64109	3.977237
H45	-3.08615	0.595689	4.797054
H46	-1.65338	2.046693	3.392612
H47	-5.91721	0.899092	-2.94445
H48	-6.54148	3.000932	-1.72466
C49	-0.91764	2.774194	0.296701
C50	-0.61853	1.557257	0.968065
C51	0.738736	1.224096	1.193638

C52	1.767572	2.06113	0.78418
C53	1.466154	3.263508	0.134389
C54	0.142629	3.608765	-0.1084
H55	0.965364	0.309312	1.733692
H56	2.800055	1.787583	0.978842
H57	2.264296	3.923917	-0.18999
H58	-0.08929	4.52791	-0.63745

Table S15. [Rh^{II}(bisq)(TFA)(TFAH)]⁺
thermodynamic values

Temp	298.15	498.15
E_{gas}	-2195.46	-2195.46
E_{solv}	-2195.53	-2195.53
G	-2195.17	-2195.24
ZPE	253.394	253.394
H_{vib}	19.860	51.663
S_{trans}	45.352	47.902
S_{rot}	37.587	39.117
S_{vib}	129.833	210.020
solv	-41.8	-41.8

Table S16. Rh^{III}(bisq)(Me_{ax})(H_{eq})(TFA_{eq}) Cartesian
coordinates

Atom	x	y	z
Rh1	-1.58291	0.17308	-1.97295
N2	-2.25752	-1.02644	0.171946
C3	-2.96656	-2.11321	-0.08034
C4	-3.42018	-3.01454	0.907718
C5	-3.1016	-2.76389	2.217945
C6	-6.19185	1.761252	-1.90071
C7	-5.7033	1.149896	-3.02993
C8	-4.34879	0.762763	-3.06822
N9	-3.50064	0.990061	-2.07152
H10	-3.18894	-2.30589	-1.12459
H11	-3.99708	-3.88572	0.615203
H12	-3.41721	-3.43306	3.014403
H13	-3.94728	0.228895	-3.92075
O14	0.279854	-0.63464	-1.73467

C15	1.258974	-0.37193	-2.53201
O16	1.307327	0.31744	-3.53923
C17	2.563093	-1.04314	-2.01902
F18	3.545299	-0.99568	-2.93196
F19	3.013282	-0.40069	-0.90787
F20	2.379384	-2.33714	-1.68358
H21	-1.18705	0.831886	-3.28369
C22	-3.93488	1.701284	-0.97122
C23	-5.31213	2.053302	-0.82826
C24	-5.74919	2.679364	0.366367
C25	-4.84742	2.967215	1.363083
C26	-3.47494	2.688666	1.18325
C27	-2.99527	2.080889	0.034851
H28	-6.80147	2.92734	0.474163
H29	-5.17914	3.442414	2.28144
H30	-2.7684	2.984768	1.951753
C31	-1.93396	-0.74692	1.476218
C32	-2.33767	-1.61586	2.542772
C33	-1.96298	-1.32964	3.880022
C34	-1.19922	-0.22339	4.160394
C35	-0.79765	0.636557	3.116153
C36	-1.15214	0.412113	1.795567
H37	-2.28417	-2.00407	4.66943
H38	-0.90274	-0.00242	5.181489
H39	-0.19676	1.510872	3.349554
H40	-6.34018	0.930402	-3.88009
H41	-7.24033	2.033915	-1.81701
C42	-1.51873	1.966058	-0.18684
C43	-0.64934	1.328195	0.741327
C44	0.728917	1.523571	0.632378
C45	1.274439	2.32086	-0.37678
C46	0.441394	2.910681	-1.31658
C47	-0.94399	2.729499	-1.22692
H48	1.387466	0.998799	1.316895
H49	2.351099	2.43768	-0.44654
H50	0.852745	3.500551	-2.12889
H51	-1.598	3.249814	-1.91899
C52	-2.01705	-1.41786	-3.19309
H53	-1.73761	-1.21383	-4.23014
H54	-1.42349	-2.25944	-2.82454

H55	-3.08539	-1.66643	-3.15044
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Table S17. Rh^{III}(bisq)(Me_{ax})(H_{eq})(TFA_{eq}) thermodynamic values

Temp	298.15	498.15
E_{gas}	-1709.37	-1709.37
E_{solv}	-1709.39	-1709.39
G	-1709.02	-1709.08
ZPE	256.697	256.697
H_{vib}	16.936	45.500
S_{trans}	44.875	47.425
S_{rot}	36.714	38.244
S_{vib}	108.681	180.630
solv	-16.6	-16.6

Table S18. Rh^{III}(bisq)(Me_{eq})(H_{ax})(TFA_{eq}) Cartesian coordinates

Atom	x	y	z
Rh1	-1.42502	0.457571	-1.90722
N2	-1.95028	-0.91697	-0.0716
C3	-2.44111	-2.09284	-0.4374
C4	-2.86431	-3.08226	0.476502
C5	-2.75228	-2.83147	1.82081
C6	-6.16116	1.587761	-1.77986
C7	-5.60067	0.986347	-2.87989
C8	-4.20699	0.784309	-2.91235
N9	-3.38706	1.167922	-1.93663
H10	-2.47494	-2.27977	-1.50401
H11	-3.25741	-4.02117	0.101023
H12	-3.06255	-3.56587	2.559994
H13	-1.78062	-0.60971	-2.916
H14	-3.74101	0.269987	-3.74385
O15	0.496779	-0.26263	-1.87087
C16	0.729073	-1.50311	-2.11625
O17	-0.03841	-2.41619	-2.40189
C18	2.247599	-1.80503	-2.0034
F19	2.517232	-3.1066	-2.1917
F20	2.954001	-1.10433	-2.91747

F21	2.719986	-1.46612	-0.77997
C22	-3.90958	1.856388	-0.85958
C23	-5.32291	2.042485	-0.73155
C24	-5.8449	2.676351	0.424311
C25	-4.99784	3.129798	1.406496
C26	-3.60118	2.99939	1.248133
C27	-3.04019	2.387426	0.139994
H28	-6.92113	2.798289	0.512379
H29	-5.39373	3.612858	2.29479
H30	-2.9397	3.409238	2.005345
C31	-1.79804	-0.65009	1.265832
C32	-2.19823	-1.60295	2.258937
C33	-2.00972	-1.31856	3.635264
C34	-1.41809	-0.14112	4.022769
C35	-1.00234	0.790711	3.047094
C36	-1.18768	0.57169	1.691567
H37	-2.32614	-2.05475	4.369757
H38	-1.26065	0.076821	5.074967
H39	-0.52203	1.712291	3.363097
H40	-6.20467	0.639207	-3.71138
H41	-7.23567	1.7288	-1.69976
C42	-1.5485	2.423495	-0.01991
C43	-0.6808	1.602868	0.738484
C44	0.703298	1.837912	0.683784
C45	1.232748	2.863299	-0.09292
C46	0.379029	3.679449	-0.83615
C47	-0.99467	3.457684	-0.79834
H48	1.364441	1.189388	1.249524
H49	2.306803	3.018956	-0.12352
H50	0.778901	4.484938	-1.44505
H51	-1.66294	4.098734	-1.36615
C52	-0.90758	1.499566	-3.5988
H53	-0.42994	0.83229	-4.32144
H54	-1.77159	1.985065	-4.06954
H55	-0.18196	2.261791	-3.29464

Table S19. Rh^{III}(bisq)(Me_{eq})(H_{ax})(TFA_{eq}) thermodynamic values

Temp	298.15	498.15
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E_{gas}	-1709.37	-1709.37
E_{solv}	-1709.39	-1709.39
G	-1709.02	-1709.08
ZPE	256.509	256.509
H_{vib}	16.489	44.663
S_{trans}	44.875	47.425
S_{rot}	36.704	38.234
S_{vib}	109.929	181.895
solv	-15.6	-15.6

Table S20. Rh^{III}(bisq)(Me_{eq})(H_{eq})(TFA_{ax}) Cartesian coordinates

Atom	x	y	z
Rh1	-1.48097	0.372491	-1.95587
N2	-2.20113	-1.10585	-0.399
C3	-2.85384	-2.21665	-0.69558
C4	-3.28819	-3.13324	0.289544
C5	-3.02281	-2.87076	1.612192
C6	-6.37967	1.610086	-1.55232
C7	-5.95338	0.873206	-2.63129
C8	-4.56786	0.64138	-2.80178
N9	-3.65649	1.128442	-1.97927
H10	-3.02837	-2.39339	-1.7529
H11	-3.81858	-4.02961	-0.01472
H12	-3.33841	-3.55586	2.394938
O13	-2.10656	-0.97039	-3.34936
H14	-4.18818	0.018417	-3.60754
H15	-0.05802	-0.20083	-1.9918
C16	-1.36032	-1.70364	-4.11549
O17	-0.15275	-1.78277	-4.2244
C18	-2.27713	-2.6246	-4.96963
F19	-1.58585	-3.35012	-5.8545
F20	-2.95327	-3.49053	-4.16709
F21	-3.20484	-1.91242	-5.65086
C22	-4.04813	1.891802	-0.91564
C23	-5.42727	2.145149	-0.64644
C24	-5.78068	2.912219	0.492186
C25	-4.80014	3.415433	1.315294
C26	-3.43467	3.189683	1.024118

C27	-3.04204	2.439595	-0.07016
H28	-6.83151	3.098265	0.698412
H29	-5.06808	4.004041	2.187766
H30	-2.67484	3.624089	1.667423
C31	-1.91947	-0.81956	0.907022
C32	-2.31564	-1.69276	1.965093
C33	-1.97384	-1.36213	3.30056
C34	-1.25655	-0.21849	3.56409
C35	-0.86119	0.636957	2.510301
C36	-1.1866	0.364751	1.192232
H37	-2.27606	-2.02872	4.104004
H38	-0.98546	0.034332	4.584926
H39	-0.28947	1.532352	2.737998
H40	-6.65628	0.453439	-3.34348
H41	-7.43756	1.7916	-1.3795
C42	-1.58008	2.329274	-0.41113
C43	-0.72425	1.3137	0.120474
C44	0.689802	1.499105	0.002688
C45	1.229663	2.630404	-0.56906
C46	0.380679	3.640508	-1.05979
C47	-0.98822	3.48635	-0.98662
H48	1.336052	0.728753	0.411753
H49	2.307782	2.74267	-0.63457
H50	0.800779	4.543598	-1.49306
H51	-1.64548	4.267742	-1.35575
C52	-0.77939	1.562327	-3.49125
H53	-0.52275	0.917333	-4.33327
H54	-1.56738	2.265674	-3.7848
H55	0.109596	2.116834	-3.18075

Table S21. Rh^{III}(bisq)(Me_{eq})(H_{eq})(TFA_{ax}) thermodynamic values

Temp	298.15	498.15
E_{gas}	-1709.36	-1709.36
E_{solv}	-1709.38	-1709.38
G	-1709.01	-1709.07
ZPE	256.617	256.617
H_{vib}	16.910	45.465
S_{trans}	44.875	47.425

S_{rot}	36.749	38.279
S_{vib}	108.249	180.176
solv	-14.8	-14.8

Table S22. Rh^{III}(bisq)(TFA)₃ Cartesian coordinates

Atom	x	y	z
Rh1	-1.641	0.351458	-1.77478
N2	-2.28889	-0.90574	-0.21433
C3	-2.92685	-2.03756	-0.4758
C4	-3.2726	-2.96037	0.531646
C5	-2.91724	-2.69463	1.831405
C6	-6.41401	1.431967	-1.7228
C7	-5.84977	0.820405	-2.81516
C8	-4.44876	0.654773	-2.87291
N9	-3.64196	1.105526	-1.92014
H10	-3.13568	-2.2313	-1.52209
H11	-3.79426	-3.87045	0.256928
H12	-3.15159	-3.39212	2.631065
O13	-2.23075	-1.07519	-3.05762
H14	-3.97195	0.134548	-3.69179
O15	0.062033	-0.74164	-1.53264
C16	1.249783	-0.52291	-2.01934
O17	1.797817	0.502726	-2.36391
C18	2.045772	-1.86155	-2.01881
F19	3.193393	-1.75049	-2.69762
F20	2.355919	-2.2037	-0.74066
F21	1.342467	-2.87974	-2.5474
O22	-0.86251	1.625491	-3.14429
C23	-1.3751	1.866839	-4.30402
O24	-2.36784	1.402053	-4.84418
C25	-0.55751	2.976428	-5.02452
F26	-0.96754	3.142141	-6.28848
F27	-0.73788	4.162333	-4.37902
F28	0.756853	2.7184	-5.03708
C29	-1.52189	-1.50131	-4.07595
O30	-0.42527	-1.18769	-4.47004
C31	-2.3682	-2.57392	-4.82148
F32	-1.68496	-3.13424	-5.8187

F33	-2.7587	-3.55731	-3.97394
F34	-3.49025	-2.01968	-5.33422
C35	-4.16674	1.811299	-0.86224
C36	-5.57739	1.953245	-0.70375
C37	-6.0791	2.621811	0.441577
C38	-5.21485	3.156781	1.368264
C39	-3.81876	3.078858	1.164355
C40	-3.28636	2.424731	0.068692
H41	-7.15443	2.713347	0.564708
H42	-5.59987	3.670622	2.243747
H43	-3.1469	3.564216	1.866113
C44	-1.91948	-0.59937	1.073221
C45	-2.2174	-1.50207	2.139902
C46	-1.78715	-1.19388	3.454843
C47	-1.07936	-0.04131	3.697456
C48	-0.79199	0.848188	2.639318
C49	-1.20563	0.601996	1.340791
H50	-2.01513	-1.88955	4.257063
H51	-0.73687	0.193242	4.700645
H52	-0.23366	1.756891	2.845087
H53	-6.45437	0.433035	-3.62771
H54	-7.49203	1.535724	-1.63078
C55	-1.82536	2.511719	-0.24032
C56	-0.85766	1.60572	0.283283
C57	0.514539	1.882456	0.052084
C58	0.912626	2.981251	-0.68549
C59	-0.04531	3.864751	-1.19698
C60	-1.39254	3.635266	-0.97001
H61	1.254484	1.198147	0.45149
H62	1.966312	3.137989	-0.88744
H63	0.261765	4.718831	-1.79158
H64	-2.13699	4.317738	-1.36791

Table S23. Rh^{III}(bisq)(TFA)₃ thermodynamic values

Temp	298.15	498.15
E_{gas}	-2721.23	-2721.23
E_{solv}	-2721.26	-2721.26
G	-2720.89	-2720.97

ZPE	264.991	264.991
H_{vib}	24.211	61.502
S_{trans}	45.818	48.368
S_{rot}	38.192	39.722
S_{vib}	160.017	254.161
solv	-23.5	-23.5

Table S24. [Rh^{III}(bisq)(TFA)₂(TFAH_{eq})]⁺ Cartesian coordinates

Atom	x	y	z
Rh1	-1.13451	0.544859	-1.47258
N2	-1.86399	-0.91533	-0.18966
C3	-2.23666	-2.11143	-0.63026
C4	-2.88015	-3.046	0.204108
C5	-3.16548	-2.70393	1.505766
C6	-5.6097	2.444338	-1.64836
C7	-5.2611	1.332486	-2.37511
C8	-3.94954	0.837737	-2.27851
N9	-3.02431	1.397643	-1.5032
H10	-2.0493	-2.3194	-1.67666
H11	-3.15732	-4.01054	-0.20565
H12	-3.68949	-3.3937	2.161235
H13	-3.63093	-0.01747	-2.86065
O14	0.60859	-0.64912	-1.35176
C15	1.798892	-0.67519	-1.72444
O16	2.480237	0.194793	-2.3397
C17	2.571953	-1.94956	-1.30441
F18	3.778045	-2.00828	-1.85638
F19	2.704379	-1.93374	0.03844
F20	1.871584	-3.03788	-1.64883
O21	-0.76488	2.058391	-2.84709
C22	0.29299	2.547384	-3.34819
O23	1.482513	2.235323	-3.18618
C24	-0.00415	3.783266	-4.24
F25	-0.39697	4.802693	-3.43757
F26	1.070771	4.171615	-4.91936
F27	-0.9975	3.523849	-5.09992
H28	1.941422	1.072078	-2.68235
C29	-3.3274	2.523605	-0.7642

C30	-4.64613	3.076242	-0.82714
C31	-4.94888	4.25232	-0.09502
C32	-3.98017	4.872124	0.65618
C33	-2.67839	4.331835	0.704488
C34	-2.33911	3.171197	0.026115
H35	-5.95394	4.658593	-0.15471
H36	-4.20473	5.778735	1.208421
H37	-1.91676	4.833789	1.294091
C39	-2.06259	-0.5654	1.124879
C40	-2.76311	-1.44073	2.006388
C41	-3.0054	-1.01804	3.338109
C42	-2.54944	0.20608	3.770678
C43	-1.80102	1.035826	2.904902
C44	-1.54646	0.666856	1.595483
H45	-3.54522	-1.67925	4.009288
H46	-2.73264	0.529025	4.790387
H47	-1.39162	1.968211	3.283005
H49	-5.96427	0.82986	-3.02907
H50	-6.61238	2.858382	-1.70279
C51	-0.93311	2.688472	0.116528
C52	-0.58335	1.46624	0.760768
C53	0.801062	1.1793	0.960639
C54	1.785004	2.057604	0.553906
C55	1.426991	3.262837	-0.07639
C56	0.095248	3.566161	-0.29805
H59	1.067401	0.259028	1.470708
H60	2.830177	1.824192	0.731331
H61	2.198133	3.956327	-0.39744
H62	-0.17841	4.482735	-0.80962
O59	-1.68769	-0.63315	-3.00618
C60	-0.91017	-0.84206	-4.04633
O61	0.198011	-0.41736	-4.27826
C62	-1.64213	-1.81782	-5.01169
F63	-2.85058	-1.32567	-5.35082
F64	-0.93532	-2.02711	-6.11446
F65	-1.83802	-3.00048	-4.38594

Table S25. [Rh^{III}(bisq)(TFA)₂(TFAH_{eq})]⁺ thermodynamic values

Temp	298.15	498.15
E _{gas}	-2721.62	-2721.62
E _{solv}	-2721.69	-2721.69
G	-2721.31	-2721.39
ZPE	272.503	272.503
H _{vib}	24.012	61.329
S _{trans}	45.822	48.372
S _{rot}	38.235	39.765
S _{vib}	157.771	251.952
solv	-42.8	-42.8

Table S26. [Rh^{III}(bisq)(κ¹-TFA_{ax})(κ²-TFA_{eq,eq})]⁺
Cartesian coordinates

Atom	x	y	z
Rh1	-1.25455	0.476184	-1.93022
N2	-2.07477	-0.92054	-0.62462
C3	-2.65238	-2.04046	-1.04676
C4	-3.33635	-2.90377	-0.16838
C5	-3.44888	-2.56521	1.160212
C6	-5.48297	2.905503	-1.52305
C7	-5.37072	1.766716	-2.28305
C8	-4.12843	1.112827	-2.35453
N9	-3.04667	1.547007	-1.7117
H10	-2.59901	-2.24081	-2.10985
H11	-3.78193	-3.80865	-0.56567
H12	-3.99991	-3.19639	1.851111
H13	-3.99609	0.23157	-2.96975
O14	-0.12459	1.585871	-3.32137
C15	0.740934	0.655497	-3.32865
O16	0.612338	-0.31334	-2.51532
C17	1.989121	0.762372	-4.21577
F18	2.936848	1.415792	-3.50087
F19	2.452362	-0.44297	-4.53292
F20	1.732135	1.459947	-5.31781
C21	-4.35108	3.403763	-0.83471
C22	-3.11623	2.688813	-0.93919
C23	-1.96059	3.193245	-0.28187
C24	-2.05968	4.378102	0.431012
C25	-3.27749	5.081016	0.544874

C26	-4.40575	4.59944	-0.07384
H27	-1.17346	4.768125	0.922971
H28	-3.31274	6.001053	1.119158
H29	-5.35013	5.130812	-0.0048
C30	-2.83188	-1.38307	1.640344
C31	-2.10328	-0.58624	0.709468
C32	-1.38278	0.552497	1.143762
C33	-1.46107	0.918307	2.476082
C34	-2.23232	0.173447	3.39777
C35	-2.88966	-0.96664	2.994826
H36	-0.89568	1.776939	2.82645
H37	-2.27482	0.490951	4.43463
H38	-3.45071	-1.56585	3.705634
H39	-6.21006	1.361699	-2.83661
H40	-6.42569	3.440197	-1.44973
C41	-0.63588	2.517119	-0.35725
C42	-0.40514	1.229104	0.221135
C43	0.934171	0.738087	0.265481
C44	1.988624	1.473634	-0.23746
C45	1.749843	2.741177	-0.79642
C46	0.462183	3.248617	-0.85836
H47	1.113416	-0.22728	0.728411
H48	2.997952	1.07757	-0.19245
H49	2.577787	3.324257	-1.18746
H50	0.280166	4.220534	-1.30453
O51	-2.13413	-0.5679	-3.42271
C52	-1.65437	-0.87979	-4.60515
O53	-0.59652	-0.61232	-5.12691
C54	-2.71553	-1.75593	-5.33433
F55	-2.89577	-2.90741	-4.64594
F56	-3.90453	-1.11763	-5.37989
F57	-2.33784	-2.05065	-6.57022

Table S27. [Rh^{III}(bisq)(κ¹-TFA_{ax})(κ²-TFA_{eq,eq})]⁺
thermodynamic values

Temp	298.15	498.15
E _{gas}	-2194.84	-2194.84
E _{solv}	-2194.90	-2194.90
G	-2194.55	-2194.62

ZPE	248.115	248.115
H_{vib}	19.155	50.643
S_{trans}	45.348	47.898
S_{rot}	37.464	38.994
S_{vib}	123.511	202.912
solv	-43.0	-43.0

Table S28. [Rh^{III}(bisq)(κ^1 -TFA_{eq})(κ^2 -TFA_{ax,eq})]⁺
Cartesian coordinates

Atom	x	y	z
Rh1	-1.2641	0.612696	-1.8913
N2	-2.28375	-0.54665	-0.46969
C3	-3.18012	-1.4588	-0.83238
C4	-3.86774	-2.25623	0.100538
C5	-3.60132	-2.09574	1.441285
C6	-5.53289	2.81993	-2.04165
C7	-5.14956	1.943364	-3.03111
C8	-3.85458	1.392147	-3.0001
N9	-2.98179	1.713192	-2.05144
H10	-3.34708	-1.57387	-1.8976
H11	-4.58561	-2.98667	-0.2548
H12	-4.10774	-2.70244	2.186552
H13	-3.51336	0.693633	-3.75378
O14	0.236269	-0.95253	-2.1362
C15	-0.47725	-1.40571	-3.06375
O16	-1.59352	-0.83049	-3.33541
C17	-0.09005	-2.66798	-3.85173
F18	-0.80839	-3.69881	-3.36811
F19	-0.37641	-2.50964	-5.14522
F20	1.205744	-2.93064	-3.70489
O21	-0.12331	1.635371	-3.21131
C22	-0.58538	2.065421	-4.35218
O23	-1.70569	1.963835	-4.81487
C24	0.536635	2.807696	-5.12998
F25	0.086992	3.274337	-6.29356
F26	0.987045	3.853881	-4.39775
F27	1.575623	1.987659	-5.36435
C29	-4.61143	3.194711	-1.03236
C30	-3.30173	2.632893	-1.08095

C31	-2.30756	3.040633	-0.15797
C32	-2.64667	3.954064	0.82353
C33	-3.95785	4.474733	0.919954
C34	-4.91865	4.115338	0.002627
H35	-1.88499	4.294269	1.518995
H36	-4.19226	5.183491	1.707638
H37	-5.91704	4.540237	0.047803
C38	-2.64925	-1.13513	1.861636
C39	-1.99943	-0.35033	0.861032
C40	-1.03121	0.618819	1.227667
C41	-0.71683	0.765614	2.56825
C42	-1.35296	-0.00614	3.566844
C43	-2.30548	-0.93671	3.223237
H44	0.036287	1.492819	2.858002
H45	-1.07988	0.140655	4.606832
H46	-2.7968	-1.53748	3.982565
H47	-5.82216	1.65662	-3.83127
H48	-6.5338	3.241418	-2.02973
C49	-0.88392	2.624427	-0.37047
C50	-0.30547	1.450266	0.210341
C51	1.1001	1.257105	0.085445
C52	1.892095	2.170187	-0.58028
C53	1.32054	3.331712	-1.13386
C54	-0.03716	3.554036	-1.02383
H55	1.540818	0.37312	0.534771
H56	2.960001	1.996205	-0.66821
H57	1.945041	4.050315	-1.65409
H58	-0.4794	4.45013	-1.44662

Table S29. [Rh^{III}(bisq)(κ^1 -TFA_{eq})(κ^2 -TFA_{ax,eq})]⁺
thermodynamic values

Temp	298.15	498.15
E_{gas}	-2194.83	-2194.83
E_{solv}	-2194.90	-2194.90
G	-2194.55	-2194.62
ZPE	247.648	247.648
H_{vib}	19.458	51.000
S_{trans}	45.348	47.898
S_{rot}	37.429	38.959

S_{vib}	125.945	205.481
solv	-43.8	-43.8

Table S30. [Rh^{III}(bisq)(Me_{ax})(TFA_{eq})(TFAH_{eq})]⁺
Cartesian coordinates

Atom	x	y	z
Rh1	-1.18717	0.471015	-1.54964
N2	-1.75493	-1.00477	-0.18766
C3	-1.93776	-2.27324	-0.53827
C4	-2.58298	-3.20744	0.293287
C5	-3.08527	-2.78538	1.502507
C6	-5.59149	2.559775	-1.37072
C7	-5.41089	1.295625	-1.87521
C8	-4.12418	0.736954	-1.84188
N9	-3.06262	1.354356	-1.32648
H10	-1.57902	-2.56244	-1.51798
H11	-2.70039	-4.22901	-0.04996
H12	-3.63784	-3.46469	2.14482
H13	-3.9561	-0.24052	-2.27002
O14	0.592518	-0.68598	-1.61934
C15	1.816629	-0.58819	-1.81732
O16	2.471932	0.344994	-2.37682
C17	2.684051	-1.73972	-1.25487
F18	3.845018	-1.84507	-1.89428
F19	2.923544	-1.47712	0.047711
F20	2.026345	-2.90248	-1.3378
O21	-0.89943	2.051633	-2.88191
C22	0.117911	2.552441	-3.44196
O23	1.310329	2.196885	-3.42451
C24	-0.21285	3.850505	-4.22483
F25	-0.48607	4.830434	-3.33079
F26	0.804474	4.24513	-4.98629
F27	-1.2953	3.678066	-4.99721
H28	1.868928	1.148947	-2.79471
C29	-3.22078	2.595489	-0.73388
C30	-4.50045	3.241669	-0.78451
C31	-4.66118	4.543112	-0.2442
C32	-3.59989	5.183457	0.344756
C33	-2.35601	4.527655	0.43788

C34	-2.14326	3.25431	-0.06995
H35	-5.63691	5.015516	-0.30587
H36	-3.71325	6.180859	0.756884
H37	-1.53458	5.024589	0.944969
C38	-2.10703	-0.59024	1.080362
C39	-2.85587	-1.45576	1.934671
C40	-3.30447	-0.96826	3.189193
C41	-2.9809	0.306161	3.591277
C42	-2.14527	1.114108	2.786778
C43	-1.69075	0.687604	1.550999
H44	-3.88829	-1.62365	3.82861
H45	-3.32006	0.680458	4.551851
H46	-1.81301	2.076434	3.164785
H47	-6.22242	0.73016	-2.31856
H48	-6.56203	3.046219	-1.40624
C49	-0.79584	2.653268	0.13335
C50	-0.59923	1.448007	0.851376
C51	0.724301	1.024136	1.11769
C52	1.820126	1.768771	0.705169
C53	1.621079	2.964756	0.004845
C54	0.333022	3.393905	-0.28108
H55	0.875496	0.10798	1.680712
H56	2.824177	1.422696	0.930314
H57	2.472129	3.553723	-0.32324
H58	0.176559	4.30563	-0.84803
C59	-1.73763	-0.55345	-3.24605
H60	-2.19906	0.173492	-3.91439
H61	-0.81482	-0.94619	-3.67557
H62	-2.42422	-1.36876	-3.01099

Table S31. [Rh^{III}(bisq)(Me_{ax})(TFA_{eq})(TFAH_{eq})]⁺
thermodynamic values

Temp	298.15	498.15
E_{gas}	-2235.35	-2235.35
E_{solv}	-2235.42	-2235.42
G	-2235.02	-2235.09
ZPE	277.623	277.623
H_{vib}	20.863	54.617
S_{trans}	45.419	47.969

S_{rot}	37.581	39.111
S_{vib}	135.292	220.408
solv	-41.3	-41.3

Table S32. [Rh^{III}(bisq)(Me_{eq})(TFA_{ax})(TFAH_{eq})]⁺
Cartesian coordinates

Atom	x	y	z
Rh1	-1.49581	0.47139	-1.98571
N2	-2.1402	-0.95727	-0.10103
C3	-2.81586	-2.03319	-0.48651
C4	-3.25288	-3.04872	0.387958
C5	-2.95613	-2.93959	1.723042
C6	-6.18449	1.57684	-1.92569
C7	-5.64147	1.016098	-3.05886
C8	-4.25925	0.750304	-3.10375
N9	-3.44891	1.056587	-2.0959
H10	-3.01301	-2.11957	-1.54896
H11	-3.79906	-3.89681	-0.01047
H12	-3.2573	-3.70556	2.432521
O13	-2.06421	-1.10118	-3.18737
H14	-3.81419	0.242337	-3.94889
O15	0.528348	-0.07166	-1.62721
C16	1.542717	-0.47926	-2.2107
O17	1.66615	-0.94326	-3.39506
C18	2.87501	-0.39197	-1.42494
F19	3.789358	-1.22612	-1.90864
F20	3.340176	0.869586	-1.51426
F21	2.661401	-0.67315	-0.13169
H22	0.758178	-1.12235	-3.89595
C23	-1.5171	-1.70418	-4.16987
O24	-0.36377	-1.63291	-4.60859
C25	-2.53197	-2.62534	-4.89796
F26	-1.95965	-3.33673	-5.86022
F27	-3.11051	-3.46183	-4.0159
F28	-3.50272	-1.85621	-5.44133
C29	-3.94691	1.673804	-0.96983
C30	-5.34498	1.915395	-0.83556
C31	-5.82799	2.46753	0.37877
C32	-4.95267	2.769675	1.396726

C33	-3.56312	2.57059	1.231025
C34	-3.04635	2.039863	0.062384
H35	-6.89395	2.64264	0.490011
H36	-5.3218	3.186424	2.328409
H37	-2.88597	2.860218	2.028481
C38	-1.8521	-0.80911	1.237299
C39	-2.2381	-1.81032	2.187057
C40	-1.8947	-1.6686	3.55591
C41	-1.18425	-0.57355	3.984137
C42	-0.80681	0.420295	3.05826
C43	-1.13104	0.334047	1.712013
H44	-2.20023	-2.44355	4.253306
H45	-0.91603	-0.4639	5.030038
H46	-0.2604	1.290349	3.410322
H47	-6.25505	0.74861	-3.91163
H48	-7.2522	1.761769	-1.85245
C49	-1.56596	1.987225	-0.17102
C50	-0.67261	1.388835	0.783096
C51	0.657808	1.784452	0.797448
C52	1.155378	2.73394	-0.11274
C53	0.330304	3.266895	-1.08693
C54	-1.02543	2.897463	-1.11752
H55	1.338625	1.313622	1.499001
H56	2.200126	3.024041	-0.06237
H57	0.706838	3.990792	-1.80234
H58	-1.70659	3.426868	-1.77451
C59	-1.00378	1.532532	-3.70105
H60	-1.00754	0.830541	-4.53445
H61	-1.73451	2.324325	-3.87499
H62	-0.00709	1.957486	-3.57383

Table S33. [Rh^{III}(bisq)(Me_{eq})(TFA_{ax})(TFAH_{eq})]⁺
thermodynamic values

Temp	298.15	498.15
E_{gas}	-2235.34	-2235.34
E_{solv}	-2235.40	-2235.40
G	-2235.01	-2235.08
ZPE	278.098	278.098
H_{vib}	20.902	54.674

S_{trans}	45.419	47.969
S_{rot}	37.667	39.197
S_{vib}	135.377	220.546
solv	-39.0	-39.0

Table S34. Rh^{III}(bisq)(Me_{ax})(TFA)₂ Cartesian coordinates

Atom	x	y	z
Rh1	-1.78997	0.294195	-1.79992
N2	-2.46201	-0.82214	-0.11724
C3	-3.3128	-1.8273	-0.28589
C4	-3.64073	-2.74979	0.724423
C5	-3.02569	-2.63263	1.945571
C6	-6.49518	1.569281	-1.7239
C7	-5.93697	1.141912	-2.90391
C8	-4.54317	0.92587	-2.97051
N9	-3.73419	1.160984	-1.94333
H10	-3.73793	-1.93411	-1.27535
H11	-4.34157	-3.54846	0.507971
H12	-3.21321	-3.34725	2.742368
H13	-4.06004	0.568767	-3.87385
O14	0.026264	-0.56132	-1.4107
C15	0.908254	-0.90885	-2.29577
O16	0.851962	-0.95849	-3.50959
C17	2.21793	-1.33722	-1.57251
F18	3.178488	-1.68023	-2.43849
F19	2.705313	-0.33224	-0.80007
F20	1.999043	-2.3948	-0.75756
O21	-0.94258	1.460991	-3.23365
C22	-1.36237	1.653121	-4.43256
O23	-2.34948	1.213168	-5.01266
C24	-0.42889	2.647813	-5.17687
F25	-0.7597	2.763765	-6.47075
F26	-0.53364	3.882494	-4.61736
F27	0.860924	2.279912	-5.10674
C28	-4.24506	1.742789	-0.80077
C29	-5.65438	1.890883	-0.62773
C30	-6.15571	2.377433	0.6075
C31	-5.28635	2.745849	1.607626

C32	-3.89046	2.701747	1.387926
C33	-3.35535	2.227277	0.203913
H34	-7.23041	2.467711	0.7391
H35	-5.666	3.119762	2.553814
H36	-3.21803	3.0877	2.148605
C37	-1.9009	-0.61564	1.127019
C38	-2.13507	-1.5582	2.180768
C39	-1.48553	-1.40308	3.43125
C40	-0.64906	-0.33597	3.644497
C41	-0.47024	0.626354	2.62982
C42	-1.08148	0.526427	1.389043
H43	-1.66465	-2.14123	4.207848
H44	-0.14061	-0.21265	4.595847
H45	0.153723	1.492951	2.826162
H46	-6.54328	0.93175	-3.77831
H47	-7.57052	1.689698	-1.62085
C48	-1.90236	2.42054	-0.11202
C49	-0.8522	1.637455	0.421996
C50	0.47959	2.001435	0.133723
C51	0.770537	3.101865	-0.65834
C52	-0.26587	3.877984	-1.18378
C53	-1.58177	3.540014	-0.9068
H54	1.280828	1.36818	0.496661
H55	1.804368	3.341781	-0.88797
H56	-0.04855	4.725586	-1.82574
H57	-2.39149	4.139594	-1.31217
C58	-2.17645	-1.25608	-3.08543
H59	-1.63658	-1.0475	-4.00399
H60	-1.79095	-2.16045	-2.61018
H61	-3.25207	-1.33489	-3.26756

Table S35. Rh^{III}(bisq)(Me_{ax})(TFA)₂ thermodynamic values

Temp	298.15	498.15
E_{gas}	-2234.96	-2234.96
E_{solv}	-2234.99	-2234.99
G	-2234.60	-2234.67
ZPE	270.508	270.508
H_{vib}	20.898	54.540

S_{trans}	45.415	47.965
S_{rot}	37.564	39.094
S_{vib}	135.543	220.398
solv	-20.8	-20.8

Table S36. Rh^{III}(bisq)(Me_{eq})(TFA)₂ Cartesian coordinates

Atom	x	y	z
Rh1	-1.46164	0.569244	-2.10035
N2	-2.25598	-0.83742	-0.15086
C3	-3.00812	-1.84918	-0.54978
C4	-3.46667	-2.87727	0.302876
C5	-3.11187	-2.8386	1.627151
C6	-6.17166	1.738522	-1.9244
C7	-5.6572	1.181766	-3.07147
C8	-4.27532	0.906124	-3.14491
N9	-3.44444	1.198366	-2.154
H10	-3.27218	-1.86454	-1.60122
H11	-4.07149	-3.68008	-0.10533
H12	-3.42571	-3.61643	2.318835
O13	-2.03275	-0.89524	-3.39064
H14	-3.83328	0.397721	-3.99501
O15	0.45035	-0.01474	-1.76219
C16	1.30052	-0.45462	-2.63279
O17	1.215068	-0.56878	-3.84185
C18	2.629594	-0.82189	-1.91298
F19	3.493271	-1.42885	-2.73588
F20	3.234155	0.306623	-1.44795
F21	2.429888	-1.6275	-0.85119
C22	-1.56589	-2.11146	-3.41281
O23	-0.7657	-2.67047	-2.69288
C24	-2.32565	-2.91679	-4.50319
F25	-1.76588	-4.10856	-4.7268
F26	-3.60157	-3.1331	-4.0736
F27	-2.40578	-2.26094	-5.67565
C28	-3.91533	1.803104	-1.0125
C29	-5.30783	2.057925	-0.84575
C30	-5.76628	2.591457	0.385779
C31	-4.87154	2.860056	1.395595

C32	-3.48798	2.642675	1.205696
C33	-2.99139	2.132244	0.019387
H34	-6.8291	2.774137	0.517867
H35	-5.22117	3.258828	2.343175
H36	-2.79512	2.895122	2.002262
C37	-1.91486	-0.75617	1.174318
C38	-2.32141	-1.76439	2.106841
C39	-1.93457	-1.67462	3.467953
C40	-1.16854	-0.61992	3.902168
C41	-0.77318	0.382909	2.992463
C42	-1.13099	0.343798	1.653877
H43	-2.2539	-2.4539	4.154686
H44	-0.86925	-0.54896	4.943671
H45	-0.17947	1.219339	3.349744
H46	-6.29252	0.924045	-3.91183
H47	-7.23621	1.931809	-1.82585
C48	-1.5134	2.035949	-0.2099
C49	-0.64133	1.38722	0.725829
C50	0.714774	1.6804	0.698425
C51	1.256213	2.589113	-0.22567
C52	0.440127	3.18596	-1.16542
C53	-0.93895	2.90163	-1.17187
H54	1.37883	1.147517	1.371278
H55	2.323332	2.785602	-0.21858
H56	0.846321	3.87497	-1.89902
H57	-1.59657	3.471611	-1.81893
C58	-0.98163	1.602971	-3.82033
H59	-0.99107	0.85572	-4.6108
H60	-1.72694	2.385844	-3.99314
H61	0.016575	2.026274	-3.71458

Table S37. Rh^{III}(bisq)(Me_{eq})(TFA)₂ thermodynamic values

Temp	298.15	498.15
E_{gas}	-2234.95	-2234.95
E_{solv}	-2234.98	-2234.98
G	-2234.59	-2234.66
ZPE	270.122	270.122
H_{vib}	21.076	54.773

S_{trans}	45.415	47.965
S_{rot}	37.573	39.103
S_{vib}	136.565	221.564
solv	-20.0	-20.0

Table S38. [Rh^{IV}(bisq)(Me_{ax})(TFA)₂]⁺ Cartesian coordinates

Atom	x	y	z
Rh1	-1.79214	0.268642	-1.78448
N2	-2.47329	-0.82548	-0.11073
C3	-3.33674	-1.82692	-0.28564
C4	-3.67802	-2.73834	0.722343
C5	-3.06574	-2.61878	1.949193
C6	-6.48896	1.53883	-1.69849
C7	-5.94482	1.05992	-2.86912
C8	-4.56038	0.824044	-2.93063
N9	-3.73975	1.089978	-1.91282
H10	-3.76354	-1.93066	-1.27444
H11	-4.3846	-3.5317	0.507391
H12	-3.26553	-3.33016	2.745515
H13	-4.09961	0.422714	-3.82442
O14	-0.01322	-0.58098	-1.45061
C15	0.903112	-0.72525	-2.37375
O16	0.831841	-0.47752	-3.56256
C17	2.222439	-1.25847	-1.7484
F18	3.137955	-1.49033	-2.68318
F19	2.711718	-0.35037	-0.87795
F20	1.981369	-2.39679	-1.07648
O21	-1.01155	1.450332	-3.14733
C22	-1.33556	1.593251	-4.41698
O23	-2.30052	1.124748	-4.98651
C24	-0.35088	2.553786	-5.13285
F25	-0.57287	2.559929	-6.44516
F26	-0.54707	3.802569	-4.65362
F27	0.92044	2.209399	-4.90129
C28	-4.23298	1.718154	-0.78273
C29	-5.64159	1.887652	-0.61818
C30	-6.13858	2.433141	0.593353
C31	-5.26751	2.834875	1.579356

C32	-3.87397	2.763113	1.363477
C33	-3.34068	2.229221	0.201864
H34	-7.21163	2.545071	0.716923
H35	-5.64368	3.256844	2.505799
H36	-3.19907	3.176491	2.107227
C37	-1.91259	-0.61337	1.136245
C38	-2.16683	-1.55471	2.187723
C39	-1.52092	-1.40825	3.441719
C40	-0.66578	-0.35529	3.657696
C41	-0.46563	0.601356	2.643162
C42	-1.07725	0.513567	1.398656
H43	-1.71479	-2.14153	4.218622
H44	-0.16051	-0.23918	4.611008
H45	0.169496	1.458498	2.844762
H46	-6.55786	0.829478	-3.73301
H47	-7.56185	1.677855	-1.59721
C48	-1.885	2.408983	-0.11057
C49	-0.83736	1.626763	0.437369
C50	0.497682	2.000934	0.170996
C51	0.795421	3.110398	-0.60684
C52	-0.23767	3.88768	-1.1403
C53	-1.55661	3.539732	-0.88909
H54	1.298979	1.381628	0.558696
H55	1.831199	3.367787	-0.80605
H56	-0.01345	4.753928	-1.75452
H57	-2.36182	4.149709	-1.28773
C58	-2.13757	-1.29462	-3.10394
H59	-1.58318	-1.0686	-4.00915
H60	-1.74563	-2.17909	-2.60221
H61	-3.20745	-1.37276	-3.29045

Table S39. [Rh^{IV}(bisq)(Me_{ax})(TFA)₂]⁺ thermodynamic values

Temp	298.15	498.15
E_{gas}	-2234.68	-2234.68
E_{solv}	-2234.75	-2234.75
G	-2234.36	-2234.43
ZPE	270.553	270.553
H_{vib}	20.834	54.490

S_{trans}	45.415	47.965
S_{rot}	37.530	39.060
S_{vib}	134.648	219.534
solv	-46.2	-46.2

Table S40. [Rh^{IV}(bisq)(Me_{eq})(TFA)₂]⁺ Cartesian coordinates

Atom	x	y	z
Rh1	-1.45323	0.550366	-2.00669
N2	-2.25008	-0.83623	-0.26674
C3	-2.99771	-1.85959	-0.66194
C4	-3.44791	-2.87578	0.200487
C5	-3.09382	-2.81389	1.526307
C6	-6.17823	1.667232	-1.89637
C7	-5.66255	1.026953	-3.00189
C8	-4.28211	0.761256	-3.05869
N9	-3.45258	1.138897	-2.09035
H10	-3.25057	-1.8952	-1.7153
H11	-4.04463	-3.68872	-0.19763
H12	-3.40268	-3.58499	2.226585
O13	-1.92927	-0.87633	-3.3776
H14	-3.83889	0.204361	-3.87689
O15	0.435538	0.16046	-1.8157
C16	1.281507	-0.40238	-2.6896
O17	1.352748	-0.12653	-3.86048
C18	2.313351	-1.30459	-1.97042
F19	2.81286	-2.20518	-2.80923
F20	3.316824	-0.51508	-1.52704
F21	1.779777	-1.92665	-0.91023
C22	-1.32975	-2.03909	-3.45993
O23	-0.36262	-2.45358	-2.85878
C24	-2.11835	-2.94743	-4.4463
F25	-1.47582	-4.08604	-4.67351
F26	-3.32434	-3.23554	-3.89003
F27	-2.34278	-2.32499	-5.61296
C28	-3.92094	1.82604	-0.99332
C29	-5.31712	2.078858	-0.84823
C30	-5.77896	2.717581	0.330974
C31	-4.88552	3.087971	1.309922

C32	-3.50057	2.868423	1.134689
C33	-3.00189	2.254694	-0.00179
H34	-6.84218	2.905047	0.447053
H35	-5.23573	3.572707	2.215538
H36	-2.80959	3.208524	1.899821
C37	-1.90662	-0.72349	1.05938
C38	-2.31054	-1.73155	1.994923
C39	-1.91524	-1.64325	3.354199
C40	-1.14245	-0.59224	3.784172
C41	-0.75042	0.40604	2.870193
C42	-1.11887	0.37352	1.53202
H43	-2.22781	-2.42439	4.041064
H44	-0.8328	-0.5208	4.821801
H45	-0.15421	1.240394	3.22751
H46	-6.2968	0.7019	-3.81871
H47	-7.24428	1.860633	-1.81431
C48	-1.51499	2.185134	-0.23201
C49	-0.6398	1.459991	0.644678
C50	0.716175	1.796805	0.673026
C51	1.232836	2.819692	-0.12431
C52	0.403452	3.525069	-0.99582
C53	-0.95158	3.217942	-1.03859
H54	1.385458	1.224405	1.306593
H55	2.291909	3.054786	-0.07161
H56	0.802039	4.318471	-1.61982
H57	-1.62132	3.812655	-1.65164
C58	-1.15192	1.745433	-3.7105
H59	-1.26852	1.053208	-4.53992
H60	-1.89227	2.542819	-3.71279
H61	-0.13369	2.118025	-3.63068

Table S41. [Rh^{IV}(bisq)(Me_{eq})(TFA)₂]⁺ thermodynamic values

Temp	298.15	498.15
E_{gas}	-2234.66	-2234.66
E_{solv}	-2234.74	-2234.74
G	-2234.35	-2234.42
ZPE	270.247	270.247
H_{vib}	21.124	54.843

S_{trans}	45.415	47.965
S_{rot}	37.509	39.039
S_{vib}	137.645	222.701
solv	-45.1	-45.1

Table S42. [Rh^{I-III}(bisq)(Me_{ax}...H_{eq})(TFA_{eq})][‡]
Cartesian coordinates

Atom	x	y	z
Rh1	-1.54145	0.302951	-2.04336
N2	-2.35754	-1.03735	0.235368
C3	-3.12297	-2.07728	-0.02826
C4	-3.59463	-2.9813	0.951589
C5	-3.22383	-2.77763	2.257934
C6	-6.19728	1.744433	-1.90362
C7	-5.70521	1.192114	-3.06234
C8	-4.34533	0.8319	-3.12939
N9	-3.49086	1.022632	-2.12898
H10	-3.38658	-2.22539	-1.07431
H11	-4.22612	-3.81519	0.661683
H12	-3.55144	-3.44992	3.046963
H13	-3.94588	0.355616	-4.0157
O14	0.326952	-0.47625	-1.75393
C15	1.294976	-0.26806	-2.57873
O16	1.318222	0.352074	-3.63275
C17	2.601939	-0.92813	-2.0585
F18	3.60646	-0.81108	-2.94014
F19	3.007945	-0.34412	-0.90266
F20	2.430871	-2.24328	-1.80438
H21	-1.31896	0.321586	-3.602
C28	-3.93908	1.655051	-0.98551
C29	-5.31713	1.988101	-0.82017
C30	-5.75019	2.540228	0.412451
C31	-4.84216	2.770492	1.419591
C32	-3.46979	2.499985	1.222869
C33	-2.99699	1.958161	0.039299
H34	-6.80316	2.77486	0.542546
H35	-5.17165	3.188155	2.366636
H36	-2.76287	2.739376	2.010564
C37	-1.98611	-0.8043	1.529056

C38	-2.39463	-1.67635	2.58965
C39	-1.96709	-1.42947	3.919037
C40	-1.15043	-0.35745	4.188928
C41	-0.74726	0.508069	3.148665
C42	-1.1482	0.321277	1.834701
H43	-2.29279	-2.09954	4.710774
H44	-0.81605	-0.16438	5.204269
H45	-0.11282	1.357851	3.383832
H46	-6.34291	1.006294	-3.92003
H47	-7.24793	2.002645	-1.80519
C48	-1.53304	1.800129	-0.2104
C49	-0.65545	1.227796	0.769691
C50	0.708482	1.475497	0.680361
C51	1.249837	2.273219	-0.34324
C52	0.429909	2.794316	-1.3244
C53	-0.9594	2.548565	-1.27824
H54	1.376064	0.998251	1.390897
H55	2.321819	2.44034	-0.37723
H56	0.83797	3.389096	-2.1347
H57	-1.61283	3.107867	-1.93918
C58	-1.7214	-1.12063	-3.67116
H59	-2.47199	-0.98718	-4.45452
H60	-0.77533	-1.41871	-4.12232
H61	-2.05621	-1.91699	-2.99531

Table S43. [Rh^{I-III}(bisq)(Me_{ax}...H_{eq})(TFA_{eq})][‡]
thermodynamic values

Temp	298.15	498.15
E_{gas}	-1709.35	-1709.35
E_{solv}	-1709.38	-1709.38
G	-1709.01	-1709.07
ZPE	255.025	255.025
H_{vib}	16.964	45.380
S_{trans}	44.875	47.425
S_{rot}	36.736	38.266
S_{vib}	109.350	180.937
solv	-15.7	-15.7

Table S44. $[\text{Rh}^{\text{I-III}}(\text{bisq})(\text{Me}_{\text{eq}}\cdots\text{H}_{\text{ax}})(\text{TFA}_{\text{eq}})]^{\ddagger}$
Cartesian coordinates

Atom	x	y	z
Rh1	-1.38971	0.228098	-1.64839
N2	-1.50615	-1.16791	0.077412
C3	-1.58648	-2.46277	-0.20942
C4	-2.06383	-3.4223	0.712167
C5	-2.49878	-3.00717	1.946999
C6	-6.14948	1.287241	-1.03634
C7	-5.6775	0.148531	-1.63902
C8	-4.28686	-0.04559	-1.71824
N9	-3.38511	0.798873	-1.2175
H10	-1.26709	-2.74002	-1.21193
H11	-2.10091	-4.46574	0.417045
H12	-2.9068	-3.71164	2.667622
H13	-1.77611	0.070141	-3.14954
H14	-3.88035	-0.915	-2.22149
O15	0.524661	-0.35648	-2.13612
C16	0.743626	-1.50022	-2.67482
O17	-0.02288	-2.43366	-2.90542
C18	2.238699	-1.65353	-3.06541
F19	2.494339	-2.85299	-3.61193
F20	2.606945	-0.71003	-3.96032
F21	3.038967	-1.52073	-1.98254
C28	-3.82812	1.928457	-0.5544
C29	-5.2334	2.213988	-0.4839
C30	-5.69142	3.411059	0.12311
C31	-4.79456	4.304538	0.652021
C32	-3.41616	4.009164	0.620188
C33	-2.91173	2.847763	0.054523
H34	-6.76049	3.602799	0.153989
H35	-5.13669	5.227964	1.109678
H36	-2.71505	4.703845	1.073433
C37	-1.84996	-0.7359	1.335325
C38	-2.40557	-1.6362	2.297375
C39	-2.83333	-1.14075	3.555186
C40	-2.69491	0.193209	3.856131
C41	-2.08539	1.068278	2.929522
C42	-1.65016	0.632769	1.68983

H43	-3.2638	-1.83372	4.272974
H44	-3.02317	0.576372	4.817904
H45	-1.92404	2.106401	3.205065
H46	-6.34245	-0.5914	-2.07114
H47	-7.21419	1.495851	-0.97498
C48	-1.43642	2.639372	0.11623
C49	-0.85527	1.566153	0.828174
C50	0.544305	1.457568	0.868423
C51	1.362106	2.396787	0.247127
C52	0.787451	3.48271	-0.4125
C53	-0.59847	3.601422	-0.47065
H54	0.989052	0.627018	1.408399
H55	2.441154	2.28313	0.285248
H56	1.415501	4.230987	-0.8874
H57	-1.0496	4.433269	-1.00404
C58	-1.2958	1.500245	-3.39019
H59	-0.74218	1.149685	-4.26482
H60	-2.23657	1.959852	-3.70277
H61	-0.67206	2.237383	-2.87442

Table S45. $[\text{Rh}^{\text{I-III}}(\text{bisq})(\text{Me}_{\text{eq}}\cdots\text{H}_{\text{ax}})(\text{TFA}_{\text{eq}})]^{\ddagger}$
thermodynamic values

Temp	298.15	498.15
E _{gas}	-1709.36	-1709.36
E _{solv}	-1709.38	-1709.38
G	-1709.01	-1709.07
ZPE	255.503	255.503
H _{vib}	16.956	45.280
S _{trans}	44.875	47.425
S _{rot}	36.789	38.319
S _{vib}	109.173	180.525
solv	-15.1	-15.1

Table S46. $[\text{Rh}^{\text{I-III}}(\text{bisq})(\text{Me}_{\text{eq}}\cdots\text{H}_{\text{eq}})(\text{TFA}_{\text{ax}})]^{\ddagger}$
Cartesian coordinates

Atom	x	y	z
Rh1	-1.42235	0.395009	-1.95056
N2	-2.44126	-0.81599	-0.4564

C3	-3.28299	-1.79926	-0.74006
C4	-3.76391	-2.69181	0.243356
C5	-3.33103	-2.56186	1.541998
C6	-6.50187	1.941264	-1.77687
C7	-6.10584	1.547452	-3.03296
C8	-4.7233	1.365678	-3.28211
N9	-3.78864	1.589681	-2.38112
H10	-3.54731	-1.9078	-1.78681
H11	-4.45412	-3.47698	-0.04647
H12	-3.66851	-3.245	2.317107
O13	-1.96626	-1.05943	-3.29279
H14	-4.38002	1.012183	-4.25278
H15	0.058683	0.318311	-2.40485
C22	-1.15115	-1.9576	-3.74226
O23	0.055026	-2.0733	-3.60673
C24	-1.93745	-3.01904	-4.56142
F25	-1.14847	-4.01388	-4.98621
F26	-2.92157	-3.57383	-3.80564
F27	-2.52845	-2.4674	-5.64387
C28	-4.15528	2.011098	-1.1371
C29	-5.52771	2.175515	-0.77175
C30	-5.85701	2.542741	0.558189
C31	-4.85581	2.743265	1.479831
C32	-3.49591	2.612427	1.108103
C33	-3.12609	2.257302	-0.17676
H34	-6.90232	2.65571	0.834283
H35	-5.10154	3.016883	2.501908
H36	-2.72582	2.803633	1.848776
C37	-2.00333	-0.65323	0.831925
C38	-2.41465	-1.53181	1.875445
C39	-1.87032	-1.35962	3.17441
C40	-0.95263	-0.36146	3.408094
C41	-0.56267	0.515265	2.36901
C42	-1.08088	0.39703	1.090268
H43	-2.17537	-2.03432	3.969077
H44	-0.52372	-0.23462	4.397829
H45	0.146453	1.310529	2.58076
H46	-6.82721	1.36127	-3.82242
H47	-7.55413	2.071131	-1.53662
C48	-1.67363	2.245003	-0.58088

C49	-0.69758	1.366071	0.015161
C50	0.687973	1.741703	-0.06581
C51	1.088484	2.902228	-0.68047
C52	0.128509	3.765766	-1.26101
C53	-1.2054	3.440343	-1.21706
H54	1.419299	1.079171	0.387536
H55	2.143565	3.15672	-0.72425
H56	0.445603	4.688	-1.73956
H57	-1.94645	4.112813	-1.63898
C58	-0.28687	1.316431	-3.54558
H59	0.092049	0.611917	-4.28687
H60	-1.14962	1.846926	-3.95838
H61	0.484189	2.039022	-3.27512

Table S47. $[\text{Rh}^{\text{III}}(\text{bisq})(\text{Me}_{\text{eq}}\cdots\text{H}_{\text{eq}})(\text{TFA}_{\text{ax}})]^{\ddagger}$
thermodynamic values

Temp	298.15	498.15
E_{gas}	-1709.34	-1709.34
E_{solv}	-1709.36	-1709.36
G	-1709.00	-1709.06
ZPE	254.865	254.865
H_{vib}	17.085	45.537
S_{trans}	44.875	47.425
S_{rot}	36.737	38.267
S_{vib}	109.824	181.503
solv	-14.5	-14.5

Table S48. $[\text{Rh}^{\text{III}}(\text{bisq})(\text{H}_{\text{ax}}\cdots\text{TFA}_{\text{eq}})(\text{Me}_{\text{eq}})]^{\ddagger}$
Cartesian coordinates

Atom	x	y	z
Rh1	-1.39565	0.495741	-1.92198
N2	-2.08353	-0.71894	-0.02223
C3	-2.79815	-1.78268	-0.36652
C4	-3.24252	-2.76625	0.541399
C5	-2.89355	-2.64306	1.862978
C6	-6.10241	1.639522	-1.95442
C7	-5.48365	1.18195	-3.09242
C8	-4.0891	0.979777	-3.08261

N9	-3.31452	1.241164	-2.02876
H10	-3.02367	-1.87202	-1.42462
H11	-3.82911	-3.60458	0.180376
H12	-3.18623	-3.38916	2.59749
H13	-1.24332	-0.91072	-3.02245
H14	-3.5816	0.561796	-3.94306
O15	0.56597	-0.44194	-1.84105
C16	0.569962	-1.38862	-2.64612
O17	-0.43395	-1.74405	-3.3621
C18	1.853737	-2.21478	-2.83324
F19	1.594452	-3.52731	-2.68479
F20	2.353855	-2.02281	-4.06801
F21	2.792374	-1.87222	-1.94127
C28	-3.89461	1.826513	-0.91296
C29	-5.31599	1.974478	-0.82421
C30	-5.90149	2.460161	0.373469
C31	-5.10916	2.816568	1.437302
C32	-3.70494	2.753299	1.316942
C33	-3.08271	2.288679	0.16922
H34	-6.98324	2.550085	0.42724
H35	-5.55283	3.185338	2.357644
H36	-3.08554	3.112929	2.132757
C37	-1.7703	-0.54044	1.304523
C38	-2.13715	-1.52266	2.284336
C39	-1.74394	-1.36794	3.637833
C40	-1.01836	-0.26781	4.021205
C41	-0.6909	0.721567	3.070875
C42	-1.05411	0.625108	1.734944
H43	-2.02573	-2.13343	4.356057
H44	-0.70713	-0.14324	5.054321
H45	-0.15003	1.605688	3.395105
H46	-6.04712	0.940029	-3.98736
H47	-7.18115	1.761726	-1.90479
C48	-1.59846	2.466367	0.054543
C49	-0.66392	1.739573	0.828215
C50	0.683091	2.1387	0.813858
C51	1.111811	3.227599	0.061393
C52	0.189728	3.947292	-0.69719
C53	-1.14905	3.568704	-0.69297
H54	1.401547	1.566287	1.392961

H55	2.160762	3.509748	0.067172
H56	0.508036	4.803231	-1.28527
H57	-1.87382	4.138042	-1.26749
C58	-0.83228	1.465937	-3.64951
H59	-0.44024	0.785822	-4.41836
H60	-1.66234	2.030452	-4.09706
H61	-0.03724	2.177549	-3.38814

Table S49. $[\text{Rh}^{\text{I-III}}(\text{bisq})(\text{H}_{\text{ax}}\cdots\text{TFA}_{\text{eq}})(\text{Me}_{\text{eq}})]^{\ddagger}$
thermodynamic values

Temp	298.15	498.15
E_{gas}	-1709.34	-1709.34
E_{solv}	-1709.36	-1709.36
G	-1708.99	-1709.05
ZPE	254.277	254.277
H_{vib}	16.882	45.262
S_{trans}	44.875	47.425
S_{rot}	36.800	38.330
S_{vib}	108.831	180.318
solv	-10.8	-10.8

Table S50. $[\text{Rh}^{\text{I-III}}(\text{bisq})(\text{H}_{\text{eq}}\cdots\text{TFA}_{\text{ax}})(\text{Me}_{\text{eq}})]^{\ddagger}$
Cartesian coordinates

Atom	x	y	z
Rh1	-1.65971	0.460815	-2.01044
N2	-2.60752	-0.84069	-0.47781
C3	-3.50406	-1.78779	-0.70465
C4	-3.94928	-2.67835	0.297772
C5	-3.42905	-2.57139	1.566751
C6	-6.64326	1.878235	-1.50803
C7	-6.33141	1.422087	-2.76684
C8	-4.96803	1.242382	-3.105
N9	-3.97216	1.504617	-2.28149
H10	-3.87672	-1.85712	-1.7226
H11	-4.68705	-3.43494	0.050575
H12	-3.74151	-3.24644	2.359507
O13	-1.84209	-1.25949	-3.41563
H14	-4.69188	0.860914	-4.08653

H15	-0.18663	-0.54857	-2.0906
C22	-0.76182	-1.87533	-3.36222
O23	0.240025	-1.55594	-2.63557
C24	-0.56209	-3.12753	-4.23232
F25	-0.14679	-4.16183	-3.47964
F26	-1.69815	-3.48702	-4.84467
F27	0.367549	-2.88795	-5.17363
C28	-4.25653	1.982626	-1.03102
C29	-5.60283	2.171431	-0.58832
C30	-5.84544	2.624726	0.734193
C31	-4.7866	2.883327	1.573313
C32	-3.45416	2.717786	1.123928
C33	-3.16719	2.272064	-0.15347
H34	-6.87111	2.760482	1.068168
H35	-4.96608	3.229334	2.587467
H36	-2.6355	2.95245	1.797965
C37	-2.08257	-0.70571	0.779181
C38	-2.46213	-1.57154	1.84603
C39	-1.84497	-1.41157	3.11317
C40	-0.89226	-0.43527	3.292777
C41	-0.53152	0.425905	2.23008
C42	-1.11434	0.316962	0.978187
H43	-2.12693	-2.07425	3.926825
H44	-0.41224	-0.31438	4.259838
H45	0.208228	1.202255	2.402306
H46	-7.10333	1.190809	-3.49438
H47	-7.67757	2.016124	-1.20172
C48	-1.74146	2.203391	-0.64813
C49	-0.75565	1.268728	-0.12527
C50	0.636532	1.631118	-0.22743
C51	1.040483	2.819157	-0.77694
C52	0.078289	3.740948	-1.26842
C53	-1.25654	3.439576	-1.2101
H54	1.368775	0.933977	0.171056
H55	2.098723	3.058755	-0.83455
H56	0.402129	4.688981	-1.68904
H57	-1.99311	4.155383	-1.56434
C58	-0.70527	1.493813	-3.52817
H59	-0.56074	0.803668	-4.36961
H60	-1.3448	2.317297	-3.86571

H61	0.263655	1.900398	-3.22573
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Table S51. $[\text{Rh}^{\text{I-III}}(\text{bisq})(\text{H}_{\text{eq}}\cdots\text{TFA}_{\text{ax}})(\text{Me}_{\text{eq}})]^{\ddagger}$
thermodynamic values

Temp	298.15	498.15
E _{gas}	-1709.33	-1709.33
E _{solv}	-1709.35	-1709.35
G	-1708.98	-1709.04
ZPE	253.851	253.851
H _{vib}	16.819	45.287
S _{trans}	44.875	47.425
S _{rot}	36.737	38.267
S _{vib}	107.196	178.908
solv	-10.4	-10.4

Table S52. $[\text{Rh}^{\text{I-III}}(\text{bisq})(\text{H}_{\text{eq}}\cdots\text{TFA}_{\text{eq}})(\text{Me}_{\text{ax}})]^{\ddagger}$
Cartesian coordinates

Atom	x	y	z
Rh1	-1.53419	0.279702	-2.02722
N2	-2.38205	-1.13052	0.475539
C3	-3.12626	-2.19585	0.262402
C4	-3.59752	-3.04646	1.291626
C5	-3.25391	-2.75549	2.58927
C6	-6.14993	1.768247	-1.98317
C7	-5.62668	1.235905	-3.13742
C8	-4.26837	0.863206	-3.17383
N9	-3.44205	1.02727	-2.14323
H10	-3.36821	-2.4082	-0.77769
H11	-4.2098	-3.90862	1.045586
H12	-3.58532	-3.38338	3.413088
H13	-3.84307	0.396393	-4.0531
O14	0.491981	-0.49509	-1.98948
C15	1.089643	-0.04498	-2.97909
O16	0.574853	0.737981	-3.85926
C17	2.576503	-0.3753	-3.17334
F18	2.883577	-0.50712	-4.47197
F19	3.321737	0.627916	-2.66327
F20	2.90853	-1.50681	-2.54141

H21	-0.51979	0.837007	-3.45351
C28	-3.92262	1.632037	-0.99657
C29	-5.30162	1.977261	-0.86721
C30	-5.76958	2.509564	0.361379
C31	-4.89381	2.710542	1.402364
C32	-3.51976	2.425325	1.245952
C33	-3.01341	1.899451	0.068711
H34	-6.82365	2.754659	0.460783
H35	-5.24899	3.116024	2.345517
H36	-2.8389	2.641113	2.062235
C37	-2.03259	-0.81717	1.755039
C38	-2.44616	-1.62203	2.864943
C39	-2.03717	-1.28054	4.179099
C40	-1.23507	-0.18304	4.384172
C41	-0.8222	0.613299	3.292392
C42	-1.20333	0.330616	1.988933
H43	-2.36255	-1.89966	5.01171
H44	-0.91617	0.081977	5.388294
H45	-0.19583	1.481188	3.47775
H46	-6.24085	1.075318	-4.0173
H47	-7.20042	2.035866	-1.91085
C48	-1.54369	1.734737	-0.13708
C49	-0.69081	1.166945	0.869579
C50	0.679045	1.401607	0.804248
C51	1.250722	2.192163	-0.20898
C52	0.447128	2.739267	-1.1898
C53	-0.94388	2.49441	-1.18211
H54	1.322703	0.938137	1.546135
H55	2.323477	2.361587	-0.21796
H56	0.871089	3.362172	-1.97186
H57	-1.57997	3.073459	-1.8425
C58	-2.0172	-1.28681	-3.2889
H59	-2.01326	-1.00028	-4.34933
H60	-1.29256	-2.09765	-3.14744
H61	-3.01829	-1.66679	-3.04272

Table S53. $[\text{Rh}^{\text{I-III}}(\text{bisq})(\text{H}_{\text{eq}}\cdots\text{TFA}_{\text{eq}})(\text{Me}_{\text{ax}})]^{\ddagger}$
thermodynamic values

Temp	298.15	498.15
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E _{gas}	-1709.34	-1709.34
E _{solv}	-1709.36	-1709.36
G	-1708.99	-1709.05
ZPE	254.423	254.423
H _{vib}	16.709	45.095
S _{trans}	44.875	47.425
S _{rot}	36.867	38.397
S _{vib}	106.470	177.969
solv	-9.4	-9.4

Table S54. $[\text{Rh}^{\text{III}}(\text{bisq})(\text{Me}_{\text{ax}}\cdots\text{H}\cdots\text{TFA}_{\text{eq}})(\text{TFA}_{\text{eq}})]^{++}$
Cartesian coordinates

Atom	x	y	z
Rh1	-2.69399	0.285886	-1.44005
N2	-1.40942	-0.78688	-0.06237
C3	-1.54868	-2.1107	-0.03647
C4	-0.83347	-2.96532	0.817107
C5	0.072866	-2.41464	1.687825
C11	-6.11308	-0.31163	2.025298
C12	-6.18577	-1.07844	0.88702
C13	-5.23064	-0.88838	-0.12968
N14	-4.26464	0.019518	-0.05771
H15	-2.26091	-2.53382	-0.72825
H16	-1.00648	-4.03408	0.763621
H17	0.654215	-3.03523	2.363709
H23	-5.26298	-1.50351	-1.01816
O28	-1.07412	0.780341	-2.63486
C29	-0.53055	-0.15564	-3.2853
O30	-0.90839	-1.3492	-3.30545
C31	0.741809	0.205367	-4.08559
F32	0.651938	-0.26279	-5.32978
F33	0.934028	1.528703	-4.12564
F34	1.800988	-0.36058	-3.4788
O35	-4.01545	1.315781	-2.60997
C36	-3.86878	1.383516	-3.90628
O37	-3.10703	0.772691	-4.6293
C38	-4.87797	2.40946	-4.49343
F39	-4.71798	2.549315	-5.80694
F40	-6.14267	2.018819	-4.24959

F41	-4.70114	3.621272	-3.91172
H42	-2.17584	-1.278	-2.81083
C43	-3.46582	-1.54068	-2.7115
H44	-3.28061	-1.84567	-3.74967
H45	-3.599	-2.42676	-2.091
H46	-4.37533	-0.95236	-2.77392
C41	0.265102	-1.01369	1.698896
C42	-0.50233	-0.19767	0.801927
C35	-0.27026	1.211344	0.799969
C44	0.692803	1.737634	1.649318
C45	1.434282	0.934739	2.538135
C46	1.22021	-0.42084	2.56397
H50	0.866907	2.809355	1.63396
H51	2.169318	1.393057	3.191629
H52	1.784718	-1.06349	3.232941
C47	-4.20032	0.846019	1.045692
C48	-5.10667	0.677825	2.137457
C49	-4.97504	1.507206	3.27997
C50	-3.99443	2.470347	3.327398
C51	-3.1358	2.66146	2.222969
C52	-3.22767	1.876221	1.086069
H55	-5.66384	1.371979	4.108421
H56	-3.89237	3.108239	4.199464
H57	-2.40401	3.463673	2.25181
H53	-6.82053	-0.44678	2.838421
H54	-6.95073	-1.83508	0.755035
C55	-0.97802	2.143118	-0.10839
C56	-2.4106	2.24267	-0.12469
C57	-3.00119	3.206193	-1.00406
C58	-2.23084	3.997872	-1.83626
C59	-0.83621	3.890014	-1.78877
C60	-0.22098	2.971478	-0.94003
H63	-4.07905	3.315627	-0.99982
H64	-2.70931	4.697265	-2.51265
H65	-0.22322	4.516341	-2.43053
H66	0.859115	2.869281	-0.94764

Table S55. $[\text{Rh}^{\text{III}}(\text{bisq})(\text{Me}_{\text{ax}}\cdots\text{H}\cdots\text{TFA}_{\text{eq}})(\text{TFA}_{\text{eq}})]^{++}$ thermodynamic values

Temp	298.15	498.15
E_{gas}	-2235.28	-2235.28
E_{solv}	-2235.35	-2235.35
G	-2234.96	-2235.03
ZPE	274.859	274.859
H_{vib}	20.208	53.616
S_{trans}	45.419	47.969
S_{rot}	37.565	39.096
S_{vib}	133.518	218.770
solv	-44.9	-44.9

Table S56. $[\text{Rh}^{\text{III}}(\text{bisq})(\text{Me}_{\text{eq}}\cdots\text{H}\cdots\text{TFA}_{\text{ax}})(\text{TFA}_{\text{eq}})]^{++}$ Cartesian coordinates

Atom	x	y	z
Rh1	-1.43905	0.089877	-1.61535
N2	-1.84068	-1.35723	-0.11465
C3	-1.94277	-2.6548	-0.36872
C4	-2.37342	-3.57588	0.608401
C5	-2.72867	-3.11801	1.856643
C11	-6.21555	1.382771	-1.44403
C12	-5.75536	0.231826	-2.03279
C13	-4.3759	-0.03051	-2.01012
N14	-3.47624	0.771321	-1.44071
H15	-1.70498	-2.972	-1.37671
H16	-2.43669	-4.62679	0.349444
H17	-3.09671	-3.8013	2.616325
H22	-3.98761	-0.92099	-2.48718
O27	0.399406	-0.80045	-1.67607
C28	1.477078	-0.25574	-2.16632
O29	1.60792	0.769779	-2.80617
C30	2.727519	-1.06627	-1.72925
F31	2.985375	-0.76363	-0.42709
F32	2.53638	-2.39139	-1.81286
F33	3.798442	-0.73947	-2.44973
H34	-0.51187	1.855912	-4.08289
H35	-0.81197	0.502513	-3.72844
O36	-1.99311	-1.37894	-2.95599
C37	-1.42284	-1.39089	-4.09226
O38	-0.71412	-0.47924	-4.55855

C39	-1.69521	-2.66013	-4.9302
F40	-1.01342	-2.64778	-6.06754
F41	-1.35071	-3.74195	-4.21356
F42	-3.01051	-2.72309	-5.19822
C43	-1.10029	1.721289	-3.16103
H44	-2.10037	2.110872	-3.35067
H45	-0.53163	2.319759	-2.46014
C41	-5.30047	2.261898	-0.81844
C42	-3.90577	1.92562	-0.80756
C35	-2.99612	2.82227	-0.16122
C44	-3.48874	3.996948	0.392788
C45	-4.8575	4.327471	0.367861
C46	-5.75036	3.467454	-0.22152
H50	-2.79307	4.669064	0.885736
H51	-5.19613	5.252891	0.822031
H52	-6.81171	3.695544	-0.24842
C47	-2.09986	-0.88068	1.143177
C48	-2.60234	-1.73953	2.162694
C49	-2.93585	-1.1771	3.421032
C50	-2.74984	0.167596	3.648439
C51	-2.18275	0.993258	2.650089
C52	-1.84521	0.486039	1.407684
H55	-3.33132	-1.8228	4.199018
H56	-3.00456	0.59803	4.611613
H57	-1.97684	2.035298	2.876359
H53	-7.27182	1.636025	-1.45133
H54	-6.41989	-0.47053	-2.523
C55	-1.54157	2.560727	-0.0596
C56	-1.04108	1.316426	0.439656
C57	0.3754	1.132901	0.489797
C58	1.251544	2.131562	0.097656
C59	0.740613	3.364991	-0.3208
C60	-0.63577	3.568975	-0.41308
H63	0.762899	0.195714	0.874075
H64	2.32107	1.956015	0.131103
H65	1.419995	4.1634	-0.60448
H66	-1.01586	4.509317	-0.7996

Table S57. $[\text{Rh}^{\text{III}}(\text{bisq})(\text{Me}_{\text{eq}}\cdots\text{H}\cdots\text{TFA}_{\text{ax}})(\text{TFA}_{\text{eq}})]^{++}$
thermodynamic values

Temp	298.15	498.15
E _{gas}	-2235.28	-2235.28
E _{solv}	-2235.35	-2235.35
G	-2234.96	-2235.03
ZPE	275.025	275.025
H _{vib}	20.769	54.513
S _{trans}	45.419	47.969
S _{rot}	37.632	39.162
S _{vib}	134.018	219.113
solv	-42.9	-42.9

Table S58. $[\text{Rh}^{\text{III}}(\text{bisq})(\text{Me}_{\text{eq}}\cdots\text{H}\cdots\text{TFA}_{\text{eq}})(\text{TFA}_{\text{ax}})]^{++}$
Cartesian coordinates

Atom	x	y	z
Rh1	-2.54666	0.080074	-1.44109
N2	-1.43029	-1.15236	-0.10785
C3	-1.62836	-2.46588	-0.09761
C4	-0.9733	-3.32677	0.803434
C5	-0.10042	-2.79624	1.722243
C11	-5.86735	0.102237	2.144461
C12	-5.94642	-0.80235	1.112812
C13	-5.00286	-0.73819	0.070596
N14	-4.04037	0.178263	0.030669
H15	-2.33006	-2.85105	-0.8266
H16	-1.17563	-4.39069	0.754252
H17	0.414261	-3.43048	2.438451
H23	-5.01481	-1.45306	-0.74354
O28	-0.98839	-0.25492	-2.76708
C29	-1.00491	0.423286	-3.83675
O30	-1.8552	1.284583	-4.14457
C31	0.202767	0.214494	-4.77504
F32	1.207044	1.005935	-4.32908
F33	0.619852	-1.0527	-4.74987
F34	-0.0897	0.56086	-6.02518
H35	-4.14741	1.813961	-3.6454
H36	-2.84475	1.178048	-3.25266
O37	-3.42724	-1.60486	-2.10772
C38	-3.5158	-1.96206	-3.37073
O39	-3.18149	-1.3701	-4.36945

C40	-4.18713	-3.36386	-3.43246
F41	-4.31314	-3.7865	-4.68316
F42	-3.44888	-4.26049	-2.7405
F43	-5.41088	-3.31185	-2.8621
C44	-4.0919	1.222421	-2.71866
H45	-4.77181	0.386496	-2.8598
H46	-4.43141	1.886432	-1.92952
C41	-3.95172	1.127729	1.025737
C42	-4.86262	1.100304	2.127793
C43	-4.74808	2.07769	3.148294
C36	-3.7845	3.054997	3.067188
C45	-2.9135	3.097535	1.957265
C46	-2.9758	2.155133	0.943584
H49	-5.44118	2.045826	3.983614
H50	-3.69803	3.80837	3.843443
H51	-2.17992	3.895574	1.88818
C48	-0.53406	-0.58825	0.770852
C49	0.147562	-1.4021	1.728848
C50	1.063632	-0.79942	2.627605
C51	1.310831	0.551377	2.563454
C52	0.661794	1.341658	1.590725
C53	-0.2539	0.799818	0.70362
H55	1.574536	-1.42608	3.352583
H56	2.018118	1.014827	3.243544
H57	0.894298	2.400695	1.525845
H53	-6.70966	-1.57168	1.083696
H54	-6.5703	0.070839	2.972031
C55	-0.81699	1.687135	-0.36288
C56	-2.08332	2.326708	-0.24948
C57	-2.37071	3.421497	-1.11309
C58	-1.46137	3.853133	-2.05713
C59	-0.22109	3.201284	-2.18547
C60	0.091492	2.142646	-1.35595
H63	-3.3166	3.940092	-0.99083
H64	-1.70055	4.698653	-2.69476
H65	0.494288	3.532077	-2.93175
H66	1.055096	1.651817	-1.43881

Table S59. $[\text{Rh}^{\text{III}}(\text{bisq})(\text{Me}_{\text{eq}}\cdots\text{H}\cdots\text{TFA}_{\text{eq}})(\text{TFA}_{\text{ax}})]^{++}$
thermodynamic values

Temp	298.15	498.15
E_{gas}	-2235.29	-2235.29
E_{solv}	-2235.36	-2235.36
G	-2234.97	-2235.04
ZPE	275.087	275.087
H_{vib}	20.163	53.503
S_{trans}	45.419	47.969
S_{rot}	37.596	39.126
S_{vib}	133.774	218.855
solv	-42.1	-42.1

Table S60. $[\text{Rh}^{\text{III}}(\text{bisq})(\text{Me}_{\text{ax}}\cdots\text{TFA}_{\text{eq}})(\text{TFA}_{\text{eq}})]^{\ddagger}$
Cartesian coordinates

Atom	x	y	z
Rh1	-1.70563	0.268794	-1.84831
N2	-2.35961	-0.81785	-0.15233
C3	-3.16198	-1.85216	-0.3833
C4	-3.55222	-2.7809	0.597609
C5	-3.0493	-2.63994	1.866887
C6	-6.37386	1.56039	-1.78431
C7	-5.82816	1.027632	-2.92775
C8	-4.43802	0.800494	-2.98108
N9	-3.61107	1.114321	-1.98652
H10	-3.49822	-1.97196	-1.40657
H11	-4.21136	-3.59871	0.327167
H12	-3.28964	-3.35237	2.651458
H13	-3.982	0.324681	-3.84282
O14	0.140998	-0.62009	-1.47396
C15	1.029362	-0.92143	-2.35376
O16	0.960029	-0.9652	-3.57613
C17	2.365242	-1.30981	-1.6598
F18	3.331144	-1.5996	-2.54297
F19	2.82152	-0.30399	-0.87313
F20	2.198387	-2.39344	-0.86525
O21	-1.00713	1.292059	-3.52121
C22	-1.29688	0.804884	-4.63096
O23	-1.94961	-0.24781	-4.89873
C24	-0.89219	1.63044	-5.8735
F25	-0.4795	0.840587	-6.87346

F26	-1.97043	2.325918	-6.30666
F27	0.079015	2.507857	-5.59665
C28	-4.1129	1.774619	-0.88065
C29	-5.52328	1.949663	-0.71912
C30	-6.02475	2.513952	0.482542
C31	-5.15649	2.921236	1.467197
C32	-3.76102	2.832723	1.262809
C33	-3.22098	2.288029	0.11042
H34	-7.0991	2.624296	0.601878
H35	-5.53503	3.35076	2.390122
H36	-3.08623	3.233729	2.013372
C37	-1.89506	-0.60294	1.129575
C38	-2.19967	-1.54848	2.165983
C39	-1.65344	-1.38821	3.46431
C40	-0.83926	-0.31861	3.73982
C41	-0.58044	0.638992	2.738387
C42	-1.09288	0.541102	1.452382
H43	-1.89074	-2.12639	4.225355
H44	-0.40739	-0.19159	4.72805
H45	0.030845	1.503301	2.979569
H46	-6.4437	0.744734	-3.77503
H47	-7.44684	1.701368	-1.68484
C48	-1.74719	2.42077	-0.14307
C49	-0.76093	1.639641	0.504368
C50	0.593392	1.957468	0.31006
C51	0.977148	3.026184	-0.49339
C52	0.005305	3.811093	-1.1135
C53	-1.3407	3.512532	-0.93183
H54	1.348617	1.320041	0.756719
H55	2.031961	3.236923	-0.64278
H56	0.292991	4.64903	-1.74169
H57	-2.10075	4.123348	-1.41029
C58	-1.96431	-1.78526	-3.69712
H59	-1.49918	-2.23645	-4.56269
H60	-1.41007	-1.93584	-2.78305
H61	-3.04119	-1.88896	-3.6475

Table S61. $[\text{Rh}^{\text{III-L}}(\text{bisq})(\text{Me}_{\text{eq}}\cdots\text{TFA}_{\text{eq}})(\text{TFA}_{\text{eq}})]^{\ddagger}$
thermodynamic values

Temp	298.15	498.15
E_{gas}	-2234.88	-2234.88
E_{solv}	-2234.90	-2234.90
G	-2234.52	-2234.59
ZPE	268.724	268.724
H_{vib}	21.152	54.690
S_{trans}	45.415	47.965
S_{rot}	37.639	39.169
S_{vib}	138.711	223.311
Solv	-16.8	-16.8

Table S62. $[\text{Rh}^{\text{III-L}}(\text{bisq})(\text{Me}_{\text{eq}}\cdots\text{TFA}_{\text{ax}})(\text{TFA}_{\text{eq}})]^{\ddagger}$
Cartesian coordinates

Atom	x	y	z
Rh1	-1.46669	0.617685	-2.26103
N2	-2.20303	-1.05256	-0.16605
C3	-2.84086	-2.13868	-0.55698
C4	-3.26628	-3.1599	0.326249
C5	-2.99254	-3.02548	1.664991
C6	-6.16685	1.853656	-2.04595
C7	-5.65664	1.406174	-3.24158
C8	-4.27885	1.123284	-3.34676
N9	-3.43298	1.281702	-2.33307
H10	-3.0145	-2.22855	-1.62693
H11	-3.78889	-4.02815	-0.06329
H12	-3.29471	-3.78667	2.380525
O13	-1.88677	-1.0843	-3.44353
H14	-3.85517	0.765394	-4.2772
O15	0.382674	-0.23981	-1.96788
C16	1.465723	0.021729	-2.59603
O17	1.695478	0.826146	-3.49793
C18	2.650565	-0.80862	-2.0286
F19	3.711613	-0.79415	-2.84923
F20	3.048101	-0.28354	-0.84011
F21	2.31659	-2.09397	-1.80861
C22	-2.02809	-0.9238	-4.67524
O23	-1.92273	0.127535	-5.35828
C24	-2.46793	-2.16758	-5.48466
F25	-1.67182	-2.35403	-6.54649

F26	-2.4546	-3.28307	-4.74368
F27	-3.73039	-1.97936	-5.92908
C28	-3.90728	1.787659	-1.14136
C29	-5.29287	2.060329	-0.94924
C30	-5.7309	2.510025	0.322492
C31	-4.82086	2.694063	1.338354
C32	-3.4436	2.462391	1.12276
C33	-2.97051	2.016315	-0.09913
H34	-6.78911	2.701784	0.477692
H35	-5.15561	3.034655	2.313918
H36	-2.74052	2.645172	1.928565
C37	-1.90685	-0.90053	1.157862
C38	-2.28809	-1.88388	2.126623
C39	-1.9444	-1.70815	3.491316
C40	-1.22542	-0.604	3.882973
C41	-0.83135	0.362075	2.930798
C42	-1.15645	0.247132	1.587734
H43	-2.2504	-2.46186	4.212836
H44	-0.95472	-0.46784	4.92615
H45	-0.26011	1.226219	3.258366
H46	-6.2916	1.250066	-4.1071
H47	-7.22797	2.055252	-1.92812
C48	-1.50862	1.857529	-0.37275
C49	-0.64739	1.239655	0.608335
C50	0.704931	1.527897	0.587526
C51	1.269714	2.406751	-0.36376
C52	0.480537	2.970887	-1.33802
C53	-0.91421	2.698437	-1.36716
H54	1.358268	1.024634	1.293479
H55	2.337523	2.599985	-0.34079
H56	0.907827	3.635305	-2.08204
H57	-1.55692	3.352515	-1.94824
C58	-0.92956	1.838978	-4.70251
H59	0.028186	1.60156	-4.23884
H60	-0.94765	1.875038	-5.78263
H61	-1.59886	2.534862	-4.21382

Table S63. $[\text{Rh}^{\text{III}}\text{I}(\text{bisq})(\text{Me}_{\text{eq}}\cdots\text{TFA}_{\text{ax}})(\text{TFA}_{\text{eq}})]^{\ddagger}$
thermodynamic values

Temp	298.15	498.15
E_{gas}	-2234.87	-2234.87
E_{solv}	-2234.90	-2234.90
G	-2234.51	-2234.58
ZPE	269.886	269.886
H_{vib}	20.634	53.968
S_{trans}	45.415	47.965
S_{rot}	37.711	39.241
S_{vib}	133.220	217.296
solv	-15.9	-15.9

Table S64. $[\text{Rh}^{\text{III}}\text{I}(\text{bisq})(\text{Me}_{\text{eq}}\cdots\text{TFA}_{\text{eq}})(\text{TFA}_{\text{ax}})]^{\ddagger}$
Cartesian coordinates

Atom	x	y	z
Rh1	-1.37399	0.681776	-2.0957
N2	-2.10779	-1.00316	-0.01336
C3	-2.73256	-2.09488	-0.4122
C4	-3.21917	-3.08447	0.476238
C5	-3.02389	-2.91349	1.824586
C6	-6.1165	1.71589	-1.8933
C7	-5.60002	1.130094	-3.02549
C8	-4.21453	0.879177	-3.10942
N9	-3.37228	1.213973	-2.13853
H10	-2.84436	-2.21117	-1.48777
H11	-3.72616	-3.9597	0.082212
H12	-3.37516	-3.65119	2.542333
O13	-1.97352	-0.91225	-3.32245
H14	-3.78021	0.354486	-3.95243
O15	0.568893	-0.01988	-2.00476
C16	1.383857	0.444199	-2.83301
O17	1.222596	1.343511	-3.69816
C18	2.828828	-0.0999	-2.72036
F19	3.420479	-0.17794	-3.91841
F20	3.55647	0.743183	-1.94857
F21	2.861767	-1.31001	-2.15016
C22	-1.31	-1.57662	-4.20372
O23	-0.20461	-1.37669	-4.68803
C24	-2.16478	-2.76654	-4.72527
F25	-1.49378	-3.54309	-5.58237

F26	-2.60152	-3.55229	-3.7118
F27	-3.26504	-2.29638	-5.36656
C28	-3.85759	1.807543	-0.99676
C29	-5.2486	2.062494	-0.827
C30	-5.69361	2.615624	0.400488
C31	-4.7879	2.889803	1.400127
C32	-3.40828	2.644911	1.212662
C33	-2.92664	2.114973	0.02854
H34	-6.75414	2.805884	0.540206
H35	-5.12897	3.305126	2.343939
H36	-2.71237	2.881833	2.010623
C37	-1.893	-0.81301	1.321411
C38	-2.33745	-1.76415	2.294469
C39	-2.07057	-1.54849	3.670612
C40	-1.36452	-0.4386	4.069589
C41	-0.91021	0.497401	3.113526
C42	-1.16401	0.344491	1.759393
H43	-2.42499	-2.27635	4.396458
H44	-1.15284	-0.27317	5.122086
H45	-0.35434	1.369235	3.447048
H46	-6.23773	0.838535	-3.85303
H47	-7.18197	1.904545	-1.79634
C48	-1.46152	1.930931	-0.2254
C49	-0.61924	1.315298	0.77618
C50	0.732321	1.603186	0.781904
C51	1.313032	2.487667	-0.15845
C52	0.540901	3.060033	-1.14116
C53	-0.85094	2.771453	-1.20945
H54	1.369372	1.108301	1.50935
H55	2.378291	2.690494	-0.10945
H56	0.977587	3.738377	-1.86656
H57	-1.48596	3.422148	-1.80311
C58	-0.55711	1.798831	-4.48404
H59	-0.55388	0.874802	-5.04613
H60	-1.49784	2.10983	-4.05118
H61	0.045656	2.608579	-4.8727

Table S65. $[\text{Rh}^{\text{III}}\text{I}(\text{bisq})(\text{Me}_{\text{eq}}\cdots\text{TFA}_{\text{eq}})(\text{TFA}_{\text{ax}})]^{\ddagger}$
thermodynamic values

Temp	298.15	498.15
E_{gas}	-2234.87	-2234.87
E_{solv}	-2234.90	-2234.90
G	-2234.52	-2234.59
ZPE	268.537	268.537
H_{vib}	20.534	53.707
S_{trans}	45.415	47.965
S_{rot}	37.709	39.239
S_{vib}	137.611	222.295
solv	-15.7	-15.7

Table S66. $[\text{Rh}^{\text{III}}\text{I}(\text{bisq})(\text{Me}_{\text{ax}}\cdots\text{TFA})(\text{TFA})_2]^{\ddagger}$
Cartesian coordinates

Atom	x	y	z
Rh1	-1.50252	0.424724	-2.02319
N2	-2.28654	-0.81943	-0.49223
C3	-3.06971	-1.83749	-0.84306
C4	-3.4507	-2.87325	0.032269
C5	-2.98102	-2.85712	1.319459
C6	-6.21954	1.435895	-2.37397
C7	-5.49754	1.16169	-3.51044
C8	-4.09427	1.040321	-3.42779
N9	-3.42239	1.214755	-2.29045
H10	-3.38596	-1.90248	-1.876
H11	-4.06595	-3.67564	-0.35953
H12	-3.20716	-3.65867	2.018553
H13	-3.4831	0.790122	-4.29211
O14	0.345533	-0.39639	-1.51862
C15	1.323086	-0.63147	-2.31642
O16	1.393293	-0.65293	-3.53748
C17	2.604473	-0.96576	-1.49468
F18	3.683271	-1.15838	-2.27438
F19	2.920738	0.029197	-0.62312
F20	2.439411	-2.0917	-0.75607
O21	-0.59378	1.706619	-3.37853
C22	-0.85026	1.807709	-4.62058
O23	-1.70369	1.256774	-5.3227
C24	0.041555	2.863722	-5.33248
F25	-0.65736	4.024388	-5.48134

F26	1.169598	3.170362	-4.66631
F27	0.398412	2.460173	-6.56814
C28	-4.10444	1.660814	-1.17338
C29	-5.53315	1.702514	-1.16178
C30	-6.21194	2.027228	0.041347
C31	-5.50121	2.349059	1.173003
C32	-4.09098	2.420419	1.124792
C33	-3.38201	2.10431	-0.02129
H34	-7.29931	2.026235	0.04412
H35	-6.01941	2.594618	2.09615
H36	-3.54237	2.7673	1.995811
C37	-1.88519	-0.71667	0.827371
C38	-2.18447	-1.76908	1.755042
C39	-1.69436	-1.71395	3.083902
C40	-0.95255	-0.63745	3.501774
C41	-0.71634	0.430294	2.614059
C42	-1.17025	0.431383	1.301858
H43	-1.92221	-2.53693	3.756784
H44	-0.56837	-0.58867	4.517039
H45	-0.17783	1.304494	2.967322
H46	-5.9826	0.987676	-4.4653
H47	-7.30621	1.470633	-2.38748
C48	-1.91984	2.429152	-0.09729
C49	-0.89764	1.659401	0.503291
C50	0.425761	2.126203	0.442422
C51	0.741918	3.326711	-0.18522
C52	-0.26903	4.097823	-0.75526
C53	-1.58551	3.651112	-0.70301
H54	1.216649	1.498901	0.838569
H55	1.778105	3.647613	-0.24465
H56	-0.03487	5.034703	-1.25297
H57	-2.37685	4.242407	-1.15526
C58	-1.70459	-1.5043	-3.68935
H59	-0.97615	-1.06292	-4.34978
H60	-1.35713	-2.09897	-2.86198
H61	-2.73525	-1.20829	-3.74942
O62	-2.01479	-3.03429	-4.7801
C63	-3.06429	-3.66626	-4.42262
O64	-3.85598	-3.45277	-3.49957
C65	-3.33485	-4.92823	-5.29462

F66	-2.78293	-6.02198	-4.71259
F67	-4.65803	-5.16887	-5.41494
F68	-2.82917	-4.83783	-6.5385

Table S67. $[\text{Rh}^{\text{III}}\text{I}(\text{bisq})(\text{Me}_{\text{ax}}\cdots\text{TFA})(\text{TFA})_2]^{\ddagger}$
thermodynamic values

Temp	298.15	498.15
E_{gas}	-2761.19	-2761.19
E_{solv}	-2761.26	-2761.26
G	-2760.86	-2760.95
ZPE	286.453	286.453
H_{vib}	25.419	64.206
S_{trans}	45.875	48.425
S_{rot}	38.831	40.361
S_{vib}	174.325	273.260
solv	-47.7	-47.7

Table S68. $[\text{Rh}^{\text{III}}\text{I}(\text{bisq})(\text{Me}_{\text{ax}}\cdots\text{TFAH})(\text{TFA})_2]^{\ddagger}$
Cartesian coordinates

Atom	x	y	z
Rh1	-1.93942	0.188279	-1.80277
N2	-2.56853	-0.8167	-0.04646
C3	-3.46219	-1.79409	-0.1765
C4	-3.7952	-2.70296	0.843188
C5	-3.14659	-2.5997	2.047501
C6	-6.51151	1.669363	-1.61815
C7	-5.98468	1.225544	-2.80706
C8	-4.60142	0.964615	-2.89272
N9	-3.76668	1.167109	-1.87438
H10	-3.92519	-1.88907	-1.14943
H11	-4.52756	-3.47824	0.646756
H12	-3.33638	-3.30259	2.85409
H13	-4.14792	0.591224	-3.80504
O14	-0.02078	-0.87409	-1.64497
C15	0.955881	-1.17016	-2.32867
O16	1.042577	-1.59569	-3.54367
C17	2.366406	-1.08481	-1.69312
F18	3.135438	-0.2217	-2.37121

F19	2.297846	-0.68086	-0.41551
F20	2.955582	-2.29217	-1.71495
O21	-1.03275	1.223993	-3.34312
C22	-1.46909	1.46489	-4.52301
O23	-2.47242	1.040504	-5.09676
C24	-0.53532	2.455118	-5.27167
F25	-0.9185	2.643589	-6.54176
F26	-0.544	3.662688	-4.65671
F27	0.739167	2.014576	-5.28304
C28	-4.23927	1.777639	-0.72787
C29	-5.64313	1.967299	-0.53765
C30	-6.11685	2.471836	0.701535
C31	-5.22679	2.823754	1.688229
C32	-3.83575	2.74534	1.448576
C33	-3.32446	2.249225	0.262232
H34	-7.18759	2.589202	0.844485
H35	-5.58499	3.211783	2.637227
H36	-3.14459	3.122099	2.196882
C37	-1.97178	-0.61974	1.189016
C38	-2.21763	-1.55176	2.253295
C39	-1.54498	-1.41932	3.494298
C40	-0.66985	-0.38205	3.696185
C41	-0.47389	0.57069	2.677131
C42	-1.10437	0.494416	1.441622
H43	-1.74175	-2.14986	4.27396
H44	-0.14738	-0.27291	4.641819
H45	0.175651	1.419702	2.865937
H46	-6.60925	1.033603	-3.67281
H47	-7.58086	1.821593	-1.49729
C48	-1.86746	2.414365	-0.05186
C49	-0.83898	1.60905	0.487864
C50	0.499354	1.946103	0.214908
C51	0.821532	3.03681	-0.58675
C52	-0.19388	3.828403	-1.1215
C53	-1.5218	3.522382	-0.84272
H54	1.287868	1.315742	0.60983
H55	1.862469	3.262278	-0.79973
H56	0.043684	4.674936	-1.75835
H57	-2.31553	4.142626	-1.24913
C58	-2.56342	-1.67087	-3.39678

H59	-2.21446	-0.95065	-4.1178
H60	-1.88966	-2.23496	-2.77397
H61	-3.61747	-1.68071	-3.16558
O62	-2.75966	-3.02905	-4.66128
C63	-1.6728	-3.2184	-5.29047
O64	-0.55123	-2.72001	-5.09675
C65	-1.76862	-4.21381	-6.47739
F66	-2.99512	-4.73975	-6.6086
F67	-1.4538	-3.59011	-7.62613
F68	-0.89821	-5.22543	-6.29666
H69	0.208322	-1.90557	-4.06165

Table S69. $[\text{Rh}^{\text{III}}\text{-(bisq)}(\text{Me}_{\text{ax}}\cdots\text{TFAH})(\text{TFA})_2]^{\ddagger}$ thermodynamic values

Temp	298.15	498.15
E_{gas}	-2761.67	-2761.67
E_{solv}	-2761.70	-2761.70
G	-2761.29	-2761.37
ZPE	294.348	294.348
H_{vib}	25.362	64.292
S_{trans}	45.879	48.429
S_{rot}	38.783	40.313
S_{vib}	172.721	271.998
solv	-18.5	-18.5

Table S70. $[\text{Rh}^{\text{III}}\text{-(bisq)}(\text{Me}_{\text{ax}}\cdots\text{TFA})(\text{TFA}_{\text{eq}})(\text{TFAH}_{\text{eq}})]^{\ddagger}$ Cartesian coordinates

Atom	x	y	z
Rh1	-1.07144	0.680948	-1.80506
N2	-1.64585	-0.9131	-0.57705
C3	-1.86278	-2.11922	-1.09477
C4	-2.54701	-3.14045	-0.40326
C5	-3.04928	-2.87856	0.846303
C6	-5.51492	2.720403	-1.50388
C7	-5.27055	1.580146	-2.22428
C8	-3.97311	1.039992	-2.20609
N9	-2.95951	1.552538	-1.51372

H10	-1.54534	-2.3039	-2.11509
H11	-2.69805	-4.08934	-0.90522
H12	-3.63139	-3.61994	1.387277
H13	-3.75648	0.164442	-2.80122
O14	0.772168	-0.40212	-1.97152
C15	1.988169	-0.19651	-2.07641
O16	2.608594	0.850892	-2.45978
C17	2.931557	-1.33821	-1.63253
F18	4.0435	-1.38108	-2.37423
F19	3.28833	-1.12162	-0.34549
F20	2.321149	-2.52579	-1.70213
O21	-0.78435	2.360469	-3.05492
C22	0.213851	3.024169	-3.42722
O23	1.439335	2.79557	-3.30938
C24	-0.14686	4.38106	-4.08377
F25	-0.33032	5.301793	-3.10343
F26	0.822687	4.826437	-4.89049
F27	-1.28475	4.306097	-4.79119
H28	1.981111	1.684104	-2.79386
C29	-3.18224	2.672721	-0.73096
C30	-4.47449	3.29911	-0.73965
C31	-4.70486	4.48398	0.003863
C32	-3.69462	5.041203	0.745364
C33	-2.43531	4.410887	0.784511
C34	-2.15385	3.244924	0.086316
H35	-5.69209	4.935816	-0.03184
H36	-3.85865	5.952399	1.312413
H37	-1.64917	4.839601	1.398614
C38	-2.01604	-0.66453	0.731525
C39	-2.79319	-1.62292	1.454462
C40	-3.26289	-1.3071	2.75453
C41	-2.94102	-0.10374	3.334919
C42	-2.09079	0.797014	2.65806
C43	-1.6103	0.538352	1.385282
H44	-3.86735	-2.03918	3.283021
H45	-3.29885	0.141185	4.330423
H46	-1.7678	1.704345	3.160116
H47	-6.03592	1.097855	-2.82189
H48	-6.49338	3.192657	-1.50676
C49	-0.77962	2.688762	0.252324

C50	-0.53295	1.425778	0.835667
C51	0.796241	1.036995	1.080581
C52	1.865861	1.864844	0.751409
C53	1.621345	3.112646	0.176724
C54	0.311983	3.517331	-0.06396
H55	0.982704	0.070186	1.539
H56	2.882674	1.532887	0.938086
H57	2.446424	3.764587	-0.09384
H58	0.119912	4.475525	-0.53716
C59	-1.57009	-0.42206	-3.88933
H60	-1.79162	0.493444	-4.41621
H61	-0.56454	-0.80875	-3.89442
H62	-2.34589	-0.99569	-3.41776
O63	-1.9351	-1.4742	-5.53631
C64	-2.16864	-2.68621	-5.21075
O65	-2.20607	-3.21124	-4.09163
C66	-2.45566	-3.62677	-6.4165
F67	-2.41493	-3.00253	-7.60513
F68	-1.55546	-4.63178	-6.44831
F69	-3.68125	-4.1813	-6.28775

Table S71. [Rh^{III}-
I(bisq)(Me_{ax}...TFA)(TFA_{eq})(TFAH_{eq})][‡]
thermodynamic values

Temp	298.15	498.15
E _{gas}	-2761.68	-2761.68
E _{solv}	-2761.72	-2761.72
G	-2761.30	-2761.39
ZPE	293.956	293.956
H _{vib}	25.269	64.098
S _{trans}	45.879	48.429
S _{rot}	38.864	40.394
S _{vib}	172.217	271.229
solv	-20.2	-20.2

Table S72. [Rh^{III}-I(bisq)(Me_{eq}...TFA)(TFA)₂][‡]
Cartesian coordinates

Atom	x	y	z
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Rh1	-1.21702	0.154439	-2.43012
N2	-2.25085	-1.16181	0.373183
C3	-2.95315	-2.27436	0.282501
C4	-3.3964	-3.00546	1.414765
C5	-3.07667	-2.54564	2.668139
C6	-5.95884	1.075012	-2.67896
C7	-5.32348	0.49617	-3.75164
C8	-3.93016	0.289527	-3.70286
N9	-3.19074	0.64696	-2.659
H10	-3.16801	-2.6127	-0.72924
H11	-3.97369	-3.91499	1.275045
H12	-3.39209	-3.07784	3.56334
O13	-1.37144	-1.44978	-3.77266
H14	-3.40269	-0.19645	-4.51523
O15	0.630838	-0.59606	-1.9053
C16	1.775128	-0.35923	-2.42655
O17	2.113859	0.388443	-3.33809
C18	2.890392	-1.1343	-1.66611
F19	4.041586	-1.1836	-2.36142
F20	3.165867	-0.51179	-0.48665
F21	2.544838	-2.40404	-1.37065
C22	-2.16222	-2.44899	-3.67301
O23	-2.98006	-2.75713	-2.80904
C24	-2.09694	-3.33353	-4.95054
F25	-2.6664	-4.53908	-4.76358
F26	-2.78316	-2.71836	-5.95326
F27	-0.84367	-3.54187	-5.39035
C28	-3.7902	1.267635	-1.58434
C29	-5.19956	1.478288	-1.55112
C30	-5.77726	2.067643	-0.39762
C31	-4.97694	2.438728	0.658211
C32	-3.57688	2.258257	0.600385
C33	-2.96627	1.679968	-0.49885
H34	-6.85369	2.216882	-0.36546
H35	-5.41753	2.89062	1.542965
H36	-2.96423	2.588413	1.432383
C37	-1.91926	-0.6859	1.603513
C38	-2.31129	-1.35842	2.805111
C39	-1.92399	-0.84046	4.066785
C40	-1.16288	0.303219	4.133317

C41	-0.7721	0.968669	2.95073
C42	-1.12983	0.508763	1.690726
H43	-2.23373	-1.36166	4.969973
H44	-0.86126	0.706316	5.096809
H45	-0.18314	1.878225	3.026379
H46	-5.87095	0.177978	-4.63261
H47	-7.03498	1.22935	-2.67852
C48	-1.47866	1.594493	-0.6264
C49	-0.63677	1.223713	0.485818
C50	0.706269	1.568328	0.442693
C51	1.266822	2.307781	-0.61947
C52	0.479414	2.700238	-1.67676
C53	-0.8932	2.341564	-1.69407
H54	1.353886	1.232366	1.246819
H55	2.326069	2.546376	-0.60273
H56	0.861577	3.287646	-2.5054
H57	-1.53456	2.875067	-2.38621
C58	-0.71496	1.280661	-4.50545
H59	-0.98732	0.440343	-5.12766
H60	-1.43297	2.050499	-4.29748
H61	0.314311	1.363954	-4.19149
O62	-0.26457	2.411053	-6.16429
C63	-0.15596	3.625024	-5.80287
O64	-0.30209	4.157015	-4.6957
C65	0.157158	4.587621	-6.99068
F66	0.841558	3.99967	-7.99266
F67	-1.00043	5.06083	-7.52471
F68	0.874224	5.660321	-6.59379

Table S73. $[\text{Rh}^{\text{III}}\text{I}(\text{bisq})(\text{Me}_{\text{eq}}\cdots\text{TFA})(\text{TFA})_2]^+$ thermodynamic values

Temp	298.15	498.15
E_{gas}	-2761.18	-2761.18
E_{solv}	-2761.26	-2761.26
G	-2760.86	-2760.95
ZPE	286.205	286.205
H_{vib}	24.891	63.306
S_{trans}	45.875	48.425
S_{rot}	38.996	40.526

S_{vib}	174.348	273.348
solv	-47.6	-47.6

Table S74. [Rh^{III}-(bisq)(Me_{eq}...TFAH)(TFA)₂]⁺
(TFAH H-bonded to TFA_{ax}) Cartesian coordinates

Atom	x	y	z
Rh1	-1.70055	0.977979	-2.23642
N2	-2.37756	-0.84403	-0.25189
C3	-3.08741	-1.86891	-0.68079
C4	-3.48321	-2.9516	0.139608
C5	-3.10944	-2.9455	1.460419
C6	-6.42178	1.915718	-1.66967
C7	-5.96357	1.506253	-2.90089
C8	-4.58161	1.302815	-3.09424
N9	-3.68843	1.505855	-2.13248
H10	-3.35039	-1.85945	-1.73236
H11	-4.0596	-3.76747	-0.28507
H12	-3.38414	-3.75868	2.128351
O13	-2.25687	-0.50881	-3.8138
H14	-4.19336	0.938079	-4.03797
O15	0.294239	0.413627	-2.26676
C16	0.644039	-0.82767	-2.26372
O17	-0.03468	-1.83743	-2.41411
C18	2.172083	-0.97212	-2.02169
F19	2.563488	-2.2517	-2.06313
F20	2.879749	-0.2886	-2.94367
F21	2.51084	-0.47964	-0.80412
C22	-1.64822	-1.32941	-4.51183
O23	-0.6654	-1.15384	-5.3195
C24	-2.22065	-2.76497	-4.60603
F25	-1.35769	-3.63435	-5.12647
F26	-2.621	-3.21831	-3.41041
F27	-3.31065	-2.7108	-5.40918
C28	-4.11511	1.93881	-0.89712
C29	-5.49725	2.139516	-0.61852
C30	-5.87693	2.522589	0.693529
C31	-4.91707	2.694801	1.665106
C32	-3.54641	2.511719	1.369014
C33	-3.12999	2.140151	0.103409

H34	-6.93029	2.667001	0.917414
H35	-5.20803	2.981902	2.671395
H36	-2.80711	2.669132	2.147712
C37	-1.99201	-0.81454	1.057218
C38	-2.3409	-1.86538	1.965236
C39	-1.91453	-1.80871	3.316552
C40	-1.14898	-0.7537	3.753734
C41	-0.78922	0.279164	2.860684
C42	-1.19439	0.278807	1.534796
H43	-2.20054	-2.61061	3.992975
H44	-0.82016	-0.70582	4.787979
H45	-0.18918	1.108436	3.225095
H46	-6.64353	1.321202	-3.72548
H47	-7.48302	2.062434	-1.48741
C48	-1.68278	2.026297	-0.26436
C49	-0.7509	1.352761	0.615132
C50	0.587223	1.686637	0.550968
C51	1.071811	2.673932	-0.34097
C52	0.21645	3.30869	-1.20706
C53	-1.16805	2.979871	-1.20058
H54	1.293411	1.143857	1.171215
H55	2.132196	2.907576	-0.34568
H56	0.58009	4.068378	-1.8924
H57	-1.86541	3.663213	-1.67538
C58	-1.053	2.302493	-4.21241
H59	-0.08764	1.910119	-3.9414
H60	-1.77235	1.68929	-4.72744
H61	-1.34157	3.297299	-3.91455
O62	-0.33138	2.988314	-5.88172
C63	0.335841	2.09385	-6.48009
O64	0.409089	0.871515	-6.25566
C65	1.235559	2.645888	-7.61894
F66	0.598228	3.590045	-8.33351
F67	2.339169	3.205751	-7.08014
F68	1.625982	1.67858	-8.45847
H69	-0.30376	-0.20041	-5.51189

Table S75. [Rh^{III}-(bisq)(Me_{eq}...TFAH)(TFA)₂]⁺
(TFAH H-bonded to TFA_{ax}) thermodynamic
values

Temp	298.15	498.15
E _{gas}	-2761.67	-2761.67
E _{solv}	-2761.70	-2761.70
G	-2761.29	-2761.37
ZPE	293.982	293.982
H _{vib}	24.724	63.294
S _{trans}	45.879	48.429
S _{rot}	38.746	40.276
S _{vib}	171.649	271.025
solv	-16.8	-16.8

Table S76. [Rh^{III}-(bisq)(Me_{eq}...TFAH)(TFA)₂][†]
(TFAH H-bonded to TFA_{eq}) Cartesian coordinates

Atom	x	y	z
Rh1	-1.52389	0.989918	-2.0052
N2	-2.12049	-0.98259	0.030936
C3	-2.68154	-2.08196	-0.43533
C4	-3.1289	-3.14094	0.392237
C5	-2.96163	-3.032	1.75117
C6	-6.28437	1.694851	-1.75691
C7	-5.71879	1.262549	-2.93353
C8	-4.32051	1.101165	-3.01653
N9	-3.51331	1.37834	-1.9974
H10	-2.77379	-2.14649	-1.51723
H11	-3.58486	-4.01883	-0.0548
H12	-3.28409	-3.82409	2.422996
O13	-2.03253	-0.58645	-3.27369
H14	-3.84621	0.699449	-3.90329
O15	0.521897	0.374824	-1.89974
C16	1.645219	0.299932	-2.39093
O17	2.16867	0.845175	-3.42961
C18	2.674437	-0.53412	-1.58673
F19	3.745642	-0.86958	-2.30832
F20	3.090907	0.199583	-0.52782
F21	2.103676	-1.65118	-1.11757
C22	-1.27473	-1.14211	-4.15719
O23	-0.16575	-0.81544	-4.55789
C24	-1.98337	-2.37934	-4.77453
F25	-1.21987	-3.00377	-5.67523

F26	-2.31401	-3.27878	-3.81609
F27	-3.13191	-2.00438	-5.38539
C28	-4.04635	1.825327	-0.80955
C29	-5.45249	1.979206	-0.6444
C30	-5.94685	2.381276	0.622439
C31	-5.07422	2.613506	1.661414
C32	-3.67965	2.475405	1.477371
C33	-3.15162	2.090412	0.25773
H34	-7.01899	2.492668	0.758276
H35	-5.45357	2.914594	2.633415
H36	-3.00977	2.68159	2.30571
C37	-1.93893	-0.85262	1.375911
C38	-2.34324	-1.87491	2.291815
C39	-2.10156	-1.71612	3.680352
C40	-1.4596	-0.59202	4.143271
C41	-1.04928	0.416396	3.241866
C42	-1.28457	0.320488	1.879988
H43	-2.42159	-2.49819	4.364748
H44	-1.26567	-0.47031	5.205057
H45	-0.54672	1.299082	3.627778
H46	-6.32498	1.026423	-3.80129
H47	-7.36047	1.811781	-1.66207
C48	-1.67579	2.033415	0.011905
C49	-0.7976	1.379911	0.956672
C50	0.536646	1.740246	0.985895
C51	1.06397	2.734768	0.127817
C52	0.25537	3.350764	-0.79712
C53	-1.12154	2.997017	-0.88625
H54	1.203567	1.223116	1.669236
H55	2.115452	2.995663	0.200988
H56	0.647512	4.129051	-1.44566
H57	-1.79369	3.662133	-1.41966
C58	-1.10403	2.314212	-4.0272
H59	-0.81863	1.348417	-4.40964
H60	-2.11782	2.670543	-4.1269
H61	-0.38806	2.918571	-3.4987
O62	-0.62948	3.123754	-5.72226
C63	0.586581	2.888494	-5.98799
O64	1.452707	2.31321	-5.30459
C65	1.069223	3.404415	-7.37099

F66	0.087972	3.990396	-8.07336
F67	2.057794	4.30578	-7.2059
F68	1.553409	2.383793	-8.10082
H69	1.620815	1.410405	-4.09482

Table S77. $[\text{Rh}^{\text{III}}\text{-(bisq)}(\text{Me}_{\text{eq}}\cdots\text{TFAH})(\text{TFA})_2]^{\dagger}$
(TFAH H-bonded to TFA_{eq}) thermodynamic values

Temp	298.15	498.15
E_{gas}	-2761.67	-2761.67
E_{solv}	-2761.70	-2761.70
G	-2761.29	-2761.37
ZPE	294.100	294.100
H_{vib}	25.342	64.303
S_{trans}	45.879	48.429
S_{rot}	38.836	40.366
S_{vib}	172.967	272.324
solv	-17.5	-17.5

Table S78. $[\text{Rh}^{\text{III}}\text{-(bisq)}(\text{Me}_{\text{eq}}\cdots\text{TFA})(\text{TFA}_{\text{ax}})(\text{TFAH}_{\text{eq}})]^{\dagger}$ Cartesian coordinates

Atom	x	y	z
Rh1	-1.48046	0.349246	-2.22855
N2	-2.18709	-1.08403	0.043352
C3	-2.89501	-2.16645	-0.22446
C4	-3.34133	-3.07787	0.761439
C5	-3.01358	-2.83917	2.073044
C6	-6.14083	1.564521	-2.05946
C7	-5.64023	0.968928	-3.19309
C8	-4.26442	0.672947	-3.27149
N9	-3.4166	0.974218	-2.2937
H10	-3.11963	-2.34196	-1.27408
H11	-3.92159	-3.94739	0.469471
H12	-3.32545	-3.51733	2.863677
O13	-2.22703	-1.35108	-3.24417
H14	-3.85311	0.14456	-4.12127
O15	0.543212	-0.29065	-1.94446

C16	1.454131	-0.95455	-2.44591
O17	1.4514	-1.69304	-3.4939
C18	2.824677	-0.88955	-1.72901
F19	3.663386	-1.8366	-2.15518
F20	3.386724	0.312785	-1.94857
F21	2.651986	-1.03658	-0.40372
H22	0.504347	-1.8301	-3.95118
C23	-1.80227	-2.14726	-4.12791
O24	-0.65963	-2.2939	-4.5986
C25	-2.92998	-3.0502	-4.6907
F26	-2.48806	-3.92582	-5.59308
F27	-3.51902	-3.73543	-3.68625
F28	-3.87952	-2.28253	-5.27304
C29	-3.87836	1.612777	-1.16407
C30	-5.26374	1.898538	-0.9974
C31	-5.69769	2.47902	0.221617
C32	-4.78557	2.76464	1.211458
C33	-3.40854	2.511093	1.017892
C34	-2.93859	1.946479	-0.15465
H35	-6.7551	2.686213	0.359273
H36	-5.1171	3.203835	2.147585
H37	-2.70324	2.775505	1.798925
C38	-1.85711	-0.81814	1.343379
C39	-2.24774	-1.69337	2.407554
C40	-1.86076	-1.40898	3.741702
C41	-1.1005	-0.2974	4.015763
C42	-0.71156	0.571146	2.972611
C43	-1.07403	0.345759	1.653067
H44	-2.17146	-2.08401	4.535101
H45	-0.79917	-0.07676	5.035543
H46	-0.12072	1.451277	3.20955
H47	-6.28202	0.70082	-4.02491
H48	-7.20116	1.778949	-1.96176
C49	-1.4755	1.787407	-0.42193
C50	-0.59131	1.253816	0.583308
C51	0.756287	1.56562	0.513105
C52	1.287613	2.372002	-0.51774
C53	0.474059	2.845265	-1.52244
C54	-0.91395	2.550202	-1.48622
H55	1.429548	1.136875	1.249587

H56	2.350984	2.589541	-0.52672
H57	0.856258	3.436261	-2.3496
H58	-1.57301	3.117223	-2.13461
C59	-0.91586	1.335511	-4.31181
H60	-0.95282	0.412326	-4.87073
H61	-1.77436	1.987444	-4.32101
H62	0.013043	1.694747	-3.9073
O63	-0.36448	2.271037	-6.03933
C64	0.372467	3.270759	-5.74704
O65	0.772087	3.669942	-4.64825
C66	0.775958	4.125593	-6.98486
F67	0.724457	3.440182	-8.14089
F68	-0.06439	5.182211	-7.09927
F69	2.023695	4.613213	-6.85394

Table S79. [Rh^{III}-

'(bisq)(Me_{eq}...TFA)(TFA_{ax})(TFAH_{eq})][‡]

thermodynamic values

Temp	298.15	498.15
E_{gas}	-2761.67	-2761.67
E_{solv}	-2761.70	-2761.70
G	-2761.29	-2761.38
ZPE	293.971	293.971
H_{vib}	25.392	64.285
S_{trans}	45.879	48.429
S_{rot}	38.924	40.454
S_{vib}	173.176	272.360
solv	-20.6	-20.6

Table S80. [Rh^{III}-

'(bisq)(Me_{eq}...TFA)(TFA_{eq})(TFAH_{ax})][‡] Cartesian

coordinates

Atom	x	y	z
Rh1	-1.31383	1.138134	-1.79542
N2	-1.96575	-0.92557	-0.05625
C3	-2.51909	-1.97869	-0.6295
C4	-2.86441	-3.16377	0.061327
C5	-2.60511	-3.23653	1.407421

C6	-6.09922	1.765886	-1.79057
C7	-5.45297	1.571633	-2.98921
C8	-4.0471	1.457405	-3.01316
N9	-3.31438	1.554013	-1.90932
H10	-2.70145	-1.89844	-1.69828
H11	-3.31449	-3.992	-0.47681
H12	-2.84281	-4.13024	1.979778
O13	-1.84871	-0.37842	-3.36404
H14	-3.51602	1.244902	-3.93247
O15	0.735598	0.767467	-1.529
C16	1.461801	-0.24194	-1.73852
O17	1.277419	-1.2468	-2.45242
C18	2.780747	-0.21953	-0.91907
F19	3.679842	-1.09205	-1.38371
F20	3.341066	1.004353	-0.91988
F21	2.511386	-0.5447	0.368919
H22	0.397332	-1.34121	-3.53401
C23	-1.37762	-1.06124	-4.28642
O24	-0.19836	-1.54038	-4.39352
C25	-2.36122	-1.53704	-5.37686
F26	-1.76329	-1.84701	-6.52001
F27	-2.97374	-2.65101	-4.89705
F28	-3.31511	-0.62252	-5.60473
C29	-3.92667	1.799605	-0.70211
C30	-5.34301	1.881624	-0.59655
C31	-5.91681	2.053078	0.689529
C32	-5.10624	2.149164	1.798063
C33	-3.69793	2.106572	1.672374
C34	-3.09534	1.939669	0.438639
H35	-6.99821	2.100606	0.78283
H36	-5.54612	2.274668	2.78303
H37	-3.07999	2.217984	2.557344
C38	-1.70948	-0.96789	1.286091
C39	-2.01142	-2.13085	2.067483
C40	-1.71322	-2.15836	3.453627
C41	-1.12309	-1.07114	4.051934
C42	-0.82119	0.078146	3.290003
C43	-1.10235	0.161636	1.934434
H44	-1.95727	-3.04913	4.027333
H45	-0.89135	-1.08619	5.113022

H46	-0.36623	0.932878	3.782524
H47	-6.00023	1.482085	-3.9212
H48	-7.18279	1.828695	-1.74377
C49	-1.61301	2.01514	0.245988
C50	-0.70829	1.369338	1.169268
C51	0.577916	1.860468	1.291928
C52	1.037679	2.967661	0.538574
C53	0.218182	3.563225	-0.38746
C54	-1.10981	3.08307	-0.56756
H55	1.272678	1.346847	1.948873
H56	2.054799	3.319109	0.681406
H57	0.560225	4.408941	-0.97607
H58	-1.82079	3.723845	-1.07956
C59	-0.74227	2.475873	-3.60593
H60	-1.04844	1.603781	-4.16191
H61	-1.41596	3.3152	-3.50913
H62	0.291161	2.613804	-3.32595
O63	-0.24517	3.136365	-5.48613
C64	-0.4746	2.19848	-6.31746
O65	-0.97451	1.079737	-6.13762
C66	-0.03973	2.579509	-7.7628
F67	1.274522	2.882971	-7.80333
F68	-0.25768	1.583236	-8.6348
F69	-0.72281	3.661626	-8.19615

Table S81. $[\text{Rh}^{\text{III}}\text{-(bisq)}(\text{Me}_{\text{eq}}\cdots\text{TFA})(\text{TFA}_{\text{eq}})(\text{TFAH}_{\text{ax}})]^{\ddagger}$
thermodynamic values

Temp	298.15	498.15
E _{gas}	-2761.67	-2761.67
E _{solv}	-2761.70	-2761.70
G	-2761.29	-2761.38
ZPE	293.817	293.817
H _{vib}	25.261	64.161
S _{trans}	45.879	48.429
S _{rot}	38.763	40.293
S _{vib}	172.157	271.363
solv	-19.7	-19.7

Table S82. $[\text{Rh}^{\text{III}}\text{-(bisq)}(\text{Me}_{\text{ax}}\cdots\text{OVCl}_3)(\text{TFA})_2]^{\ddagger}$
Cartesian coordinates

Atom	x	y	z
Rh1	-1.58785	0.147123	-2.15456
N2	-2.40284	-0.98379	-0.55175
C3	-3.27834	-1.95634	-0.78307
C4	-3.69731	-2.87488	0.196918
C5	-3.15833	-2.78164	1.456087
C6	-6.28667	1.408815	-2.32183
C7	-5.68334	0.939556	-3.46355
C8	-4.28698	0.733001	-3.4699
N9	-3.51953	1.004979	-2.41941
H10	-3.65966	-2.04262	-1.79314
H11	-4.39852	-3.65433	-0.07744
H12	-3.4184	-3.49566	2.232782
H13	-3.77389	0.345709	-4.34439
O14	0.197607	-0.75992	-1.6713
C15	1.166935	-1.02343	-2.49072
O16	1.213278	-0.98607	-3.70778
C17	2.42401	-1.47128	-1.69211
F18	3.428073	-1.82116	-2.50068
F19	2.870193	-0.46621	-0.89416
F20	2.143255	-2.52218	-0.89293
O21	-0.668	1.332741	-3.5331
C22	-1.00603	1.362033	-4.77402
O23	-1.89626	0.748447	-5.35358
C24	-0.12404	2.366897	-5.56099
F25	-0.42289	2.367528	-6.8657
F26	-0.32824	3.623548	-5.08986
F27	1.183057	2.089378	-5.42691
C28	-4.07788	1.602595	-1.30902
C29	-5.49086	1.763621	-1.20234
C30	-6.0377	2.282367	-0.00039
C31	-5.20992	2.658547	1.031638
C32	-3.80625	2.582993	0.881512
C33	-3.22882	2.077835	-0.26874
H34	-7.11607	2.385898	0.083184
H35	-5.62779	3.055478	1.951832
H36	-3.16296	2.963158	1.669728

C37	-1.916	-0.80238	0.726051
C38	-2.25143	-1.73653	1.757266
C39	-1.67853	-1.60074	3.047225
C40	-0.82053	-0.56254	3.314854
C41	-0.53966	0.391371	2.314839
C42	-1.0753	0.309257	1.038466
H43	-1.93153	-2.33093	3.810657
H44	-0.37125	-0.45586	4.297421
H45	0.101291	1.235021	2.552539
H46	-6.25395	0.684169	-4.34933
H47	-7.3656	1.52747	-2.2656
C48	-1.7571	2.222266	-0.51482
C49	-0.75757	1.408583	0.082868
C50	0.59878	1.752725	-0.10966
C51	0.961259	2.853648	-0.86766
C52	-0.02399	3.657208	-1.45443
C53	-1.36062	3.344956	-1.27287
H54	1.36132	1.104893	0.305742
H55	2.012289	3.0785	-1.02214
H56	0.254263	4.510236	-2.06523
H57	-2.12946	3.965431	-1.72316
C58	-1.70363	-1.74025	-3.6114
H59	-0.86953	-1.41674	-4.21774
H60	-1.52169	-2.44935	-2.81693
H61	-2.70712	-1.42034	-3.84891
O62	-2.03151	-3.29969	-4.90712
V63	-3.35456	-4.22706	-4.75832
Cl64	-3.23687	-5.19915	-2.78218
Cl65	-5.08681	-2.8542	-4.66875
Cl66	-3.58981	-5.69025	-6.33775

Table S83. $[\text{Rh}^{\text{III-IV}}(\text{bisq})(\text{Me}_{\text{ax}}\cdots\text{OVCl}_3)(\text{TFA})_2]^{\ddagger}$ thermodynamic values

Temp	298.15	498.15
E_{gas}	-3762.25	-3762.25
E_{solv}	-3762.28	-3762.28
G	-3761.90	-3761.99
ZPE	274.581	274.581
H_{vib}	25.976	64.413

S_{trans}	46.090	48.640
S_{rot}	39.006	40.536
S_{vib}	178.086	276.222
solv	-19.3	-19.3

Table S84. $[\text{Rh}^{\text{III-}}\text{II}(\text{bisq})(\text{Me}_{\text{ax}}\cdots\text{OVCl}_3)(\text{TFA}_{\text{eq}})(\text{TFAH}_{\text{eq}})]^{+\ddagger}$ Cartesian coordinates

Atom	x	y	z
Rh1	-1.34911	0.180995	-1.44333
N2	-1.81265	-1.19378	0.048578
C3	-1.96675	-2.49025	-0.20105
C4	-2.57219	-3.37307	0.712982
C5	-3.06413	-2.87029	1.896635
C6	-5.7673	2.25422	-1.28856
C7	-5.58518	0.940865	-1.64668
C8	-4.2914	0.403132	-1.57431
N9	-3.22403	1.084092	-1.16048
H10	-1.60745	-2.84375	-1.16104
H11	-2.66837	-4.42138	0.453694
H12	-3.58607	-3.51256	2.600422
H13	-4.12411	-0.61918	-1.8842
O14	0.389483	-1.01959	-1.69656
C15	1.617039	-0.86535	-1.84958
O16	2.250308	0.156501	-2.25663
C17	2.504424	-2.06597	-1.44427
F18	3.705616	-2.01057	-2.01116
F19	2.650421	-2.03823	-0.10379
F20	1.907479	-3.21577	-1.78322
O21	-1.16009	1.610883	-2.96341
C22	-0.15576	2.211931	-3.44267
O23	1.06125	2.006157	-3.27029
C24	-0.53473	3.426959	-4.32772
F25	-0.91976	4.436832	-3.51098
F26	0.49184	3.846437	-5.06343
F27	-1.56059	3.129989	-5.13758
H28	1.630074	0.973624	-2.63967
C29	-3.38573	2.378901	-0.70365
C30	-4.67284	3.005262	-0.80139

C31	-4.83825	4.357381	-0.40627
C32	-3.77439	5.066021	0.093044
C33	-2.523	4.434255	0.238249
C34	-2.30242	3.11528	-0.1337
H35	-5.81909	4.812852	-0.50446
H36	-3.8912	6.101465	0.396217
H37	-1.70169	4.990743	0.679268
C38	-2.15938	-0.69007	1.283091
C39	-2.86812	-1.50374	2.217699
C40	-3.31888	-0.92199	3.431512
C41	-3.03897	0.395227	3.710975
C42	-2.24321	1.159335	2.825854
C43	-1.7846	0.638583	1.629312
H44	-3.87169	-1.53549	4.137068
H45	-3.38269	0.842152	4.638386
H46	-1.94548	2.163781	3.111985
H47	-6.39912	0.32199	-2.00637
H48	-6.74216	2.727367	-1.36405
C49	-0.94583	2.552556	0.102968
C50	-0.72381	1.365252	0.85054
C51	0.60944	0.965994	1.109542
C52	1.690896	1.716155	0.669039
C53	1.466641	2.892743	-0.05392
C54	0.167841	3.294158	-0.33887
H55	0.778279	0.070626	1.700583
H56	2.702863	1.394078	0.894679
H57	2.304342	3.486727	-0.40636
H58	-0.00298	4.184408	-0.93606
C59	-2.08927	-1.13055	-3.44183
H60	-2.51069	-0.19594	-3.78165
H61	-1.04526	-1.34677	-3.61825
H62	-2.65691	-1.79094	-2.80564
O63	-2.68263	-2.10373	-4.96901
V64	-2.34562	-1.7066	-6.5218
Cl65	-3.16808	-3.17374	-7.84514
Cl66	-3.20792	0.244137	-6.84422
Cl67	-0.19198	-1.62743	-6.65053

Table S85. [Rh^{III}-

^{II}(bisq)(Me_{ax}...OVCl₃)(TFA_{eq})(TFAH_{eq})]⁺⁺

thermodynamic values

Temp	298.15	498.15
E_{gas}	-3762.64	-3762.64
E_{solv}	-3762.70	-3762.70
G	-3762.31	-3762.39
ZPE	281.632	281.632
H_{vib}	25.878	64.400
S_{trans}	46.093	48.643
S_{rot}	39.076	40.606
S_{vib}	177.134	275.454
solv	-38.0	-38.0

Table S86. [Rh^{III-II}(bisq)(Me_{eq}...OVCl₃)(TFA)₂]⁺

Cartesian coordinates

Atom	x	y	z
Rh1	-1.34816	0.250775	-2.12771
N2	-2.12246	-0.95169	-0.36607
C3	-2.83298	-2.02343	-0.68311
C4	-3.32715	-2.92977	0.277607
C5	-3.05006	-2.70418	1.602374
C6	-5.94685	1.83569	-2.2854
C7	-5.45006	1.099028	-3.33436
C8	-4.09239	0.716251	-3.32766
N9	-3.25662	1.080993	-2.36294
H10	-2.9921	-2.19107	-1.74301
H11	-3.90037	-3.79023	-0.05018
H12	-3.40135	-3.38377	2.374381
O13	-1.9877	-1.23546	-3.3804
H14	-3.68346	0.062232	-4.08903
O15	0.388005	-0.76963	-1.73955
C16	1.554785	-0.44693	-2.17949
O17	1.912212	0.50881	-2.85549
C18	2.64066	-1.41354	-1.63516
F19	3.741799	-1.39847	-2.39417
F20	2.996737	-1.00514	-0.38511
F21	2.215125	-2.68356	-1.53633

C22	-1.24321	-1.92836	-4.19955
O23	-0.09549	-1.76486	-4.55165
C24	-2.09558	-3.08999	-4.78404
F25	-1.3819	-3.87668	-5.58895
F26	-2.60999	-3.85826	-3.79272
F27	-3.13921	-2.59517	-5.49022
C28	-3.70622	1.873919	-1.33246
C29	-5.08136	2.237473	-1.23648
C30	-5.51946	2.971223	-0.10492
C31	-4.62251	3.331982	0.873882
C32	-3.25158	3.014435	0.740012
C33	-2.77663	2.305807	-0.34913
H34	-6.56902	3.240455	-0.02666
H35	-4.9571	3.889002	1.743758
H36	-2.55021	3.357081	1.494481
C37	-1.82059	-0.69292	0.946795
C38	-2.27731	-1.57725	1.976957
C39	-1.93481	-1.32797	3.329664
C40	-1.14971	-0.24981	3.656461
C41	-0.69074	0.617207	2.642983
C42	-1.01398	0.431692	1.307704
H43	-2.29436	-2.011	4.093941
H44	-0.87683	-0.05846	4.689704
H45	-0.07114	1.467008	2.913825
H46	-6.08154	0.781611	-4.15661
H47	-6.99622	2.115013	-2.24507
C48	-1.2972	2.141372	-0.56709
C49	-0.46355	1.38932	0.31204
C50	0.922475	1.615198	0.296566
C51	1.492181	2.558365	-0.55241
C52	0.691913	3.295121	-1.4292
C53	-0.68013	3.089354	-1.43069
H54	1.56114	1.007478	0.928641
H55	2.568475	2.698449	-0.55057
H56	1.129225	4.019482	-2.10807
H57	-1.31175	3.698323	-2.07059
C58	-0.63289	1.436886	-4.26384
H59	-0.96152	0.59632	-4.85691
H60	-1.37752	2.15295	-3.94992
H61	0.322994	1.35279	-3.74949

O62	0.035635	2.398354	-5.64137
V63	-0.7506	3.692073	-6.28549
Cl64	-0.98688	5.188947	-4.68241
Cl65	0.39344	4.538093	-7.92651
Cl66	-2.70693	2.984	-6.97912

Table S87. $[\text{Rh}^{\text{III-IV}}(\text{bisq})(\text{Me}_{\text{eq}}\cdots\text{OVCl}_3)(\text{TFA})_2]^{\ddagger}$ thermodynamic values

Temp	298.15	498.15
E_{gas}	-3762.22	-3762.22
E_{solv}	-3762.27	-3762.27
G	-3761.89	-3761.97
ZPE	274.641	274.641
H_{vib}	26.655	65.437
S_{trans}	46.090	48.640
S_{rot}	39.064	40.594
S_{vib}	179.812	277.815
solv	-31.1	-31.1

Table S88. $[\text{Rh}^{\text{III-IV}}(\text{bisq})(\text{Me}_{\text{eq}}\cdots\text{OVCl}_3)(\text{TFA}_{\text{ax}})(\text{TFAH}_{\text{eq}})]^{+\ddagger}$ Cartesian coordinates

Atom	x	y	z
Rh1	-1.83835	0.62965	-1.88692
N2	-2.33283	-0.89151	-0.11163
C3	-2.9549	-1.99051	-0.52107
C4	-3.32416	-3.04433	0.33803
C5	-3.01755	-2.94288	1.672146
C6	-6.56062	1.611635	-1.61093
C7	-6.06191	1.01373	-2.74561
C8	-4.67854	0.772434	-2.84992
N9	-3.82223	1.134933	-1.8988
H10	-3.15827	-2.05863	-1.58369
H11	-3.8282	-3.9134	-0.0703
H12	-3.27011	-3.73698	2.369369
O13	-2.35941	-0.89673	-3.21134
H14	-4.26652	0.241275	-3.69804
O15	0.24196	0.184666	-1.66974

C16	1.259113	-0.11082	-2.31363
O17	1.365334	-0.47877	-3.53369
C18	2.617462	0.016366	-1.57978
F19	3.547755	-0.75743	-2.12841
F20	3.016564	1.301137	-1.64823
F21	2.473135	-0.31478	-0.28861
H22	0.452939	-0.67415	-4.01328
C23	-1.80167	-1.39632	-4.24324
O24	-0.68017	-1.18257	-4.72049
C25	-2.75221	-2.36919	-4.98898
F26	-2.16208	-2.95174	-6.02391
F27	-3.19557	-3.31664	-4.14144
F28	-3.82354	-1.67144	-5.43153
C29	-4.28141	1.774214	-0.76732
C30	-5.67559	2.002182	-0.5759
C31	-6.10929	2.596377	0.636898
C32	-5.19323	2.94631	1.602476
C33	-3.81081	2.751356	1.382224
C34	-3.34189	2.183447	0.210558
H35	-7.17087	2.766906	0.788736
H36	-5.52464	3.398022	2.532021
H37	-3.10033	3.077715	2.135733
C38	-2.02733	-0.74828	1.221685
C39	-2.35181	-1.78892	2.152919
C40	-1.99495	-1.66154	3.519715
C41	-1.32549	-0.54634	3.960649
C42	-1.00318	0.480763	3.050236
C43	-1.34598	0.414525	1.707814
H44	-2.25437	-2.46444	4.203756
H45	-1.04448	-0.44674	5.004121
H46	-0.48329	1.362741	3.412937
H47	-6.71015	0.702468	-3.55681
H48	-7.62651	1.785642	-1.49449
C49	-1.87098	2.145334	-0.08625
C50	-0.93822	1.516979	0.807579
C51	0.386432	1.941886	0.807415
C52	0.834329	2.950194	-0.05907
C53	-0.03284	3.525039	-0.97846
C54	-1.37619	3.131499	-0.98623
H55	1.096457	1.450203	1.464035

H56	1.873491	3.26169	-0.02338
H57	0.307627	4.297828	-1.66
H58	-2.08943	3.683024	-1.59056
C59	-1.44288	1.970942	-3.9629
H60	-0.42576	2.019887	-3.60475
H61	-1.75951	1.138051	-4.56691
H62	-2.15966	2.726188	-3.68073
O63	-0.97835	2.939646	-5.59117
V64	0.127564	4.143823	-5.60604
Cl65	0.546159	4.794459	-7.60119
Cl66	-0.70453	5.724262	-4.36208
Cl67	1.898313	3.329033	-4.63781

Table S89. [Rh^{III}-
^{II}(bisq)(Me_{eq}...OVCl₃)(TFA_{ax})(TFAH_{eq})]⁺⁺
thermodynamic values

Temp	298.15	498.15
E_{gas}	-3762.63	-3762.63
E_{solv}	-3762.69	-3762.69
G	-3762.30	-3762.38
ZPE	282.077	282.077
H_{vib}	26.061	64.635
S_{trans}	46.093	48.643
S_{rot}	39.096	40.626
S_{vib}	179.516	277.980
solv	-37.1	-37.1

Table S90. [Rh^{III}-
^{II}(bisq)(Me_{eq}...OVCl₃)(TFA_{eq})(TFAH_{ax})]⁺⁺ Cartesian
coordinates

Atom	x	y	z
Rh1	-1.74828	0.646494	-1.83095
N2	-2.3234	-0.86226	-0.07378
C3	-2.96478	-1.94331	-0.49857
C4	-3.33422	-3.01359	0.339197
C5	-3.00581	-2.94737	1.670587
C6	-6.48345	1.669861	-1.67947
C7	-5.96101	1.10783	-2.82222

C8	-4.57722	0.857968	-2.89757
N9	-3.7413	1.180194	-1.91557
H10	-3.18761	-1.98594	-1.55862
H11	-3.854	-3.86717	-0.08181
H12	-3.25536	-3.75605	2.351927
O13	-2.21601	-0.89974	-3.24952
H14	-4.15031	0.351834	-3.75442
O15	0.241061	0.146089	-1.47992
C16	1.205279	-0.08332	-2.26393
O17	1.191659	-0.28239	-3.49654
C18	2.59529	-0.04881	-1.57416
F19	3.486193	-0.7843	-2.23524
F20	3.027582	1.230828	-1.5422
F21	2.517488	-0.49262	-0.30904
H22	0.153232	-0.89867	-4.13851
C23	-1.72319	-1.54031	-4.19911
O24	-0.54546	-1.50557	-4.67187
C25	-2.71072	-2.48603	-4.92273
F26	-2.12677	-3.20302	-5.87115
F27	-3.27061	-3.30921	-4.01948
F28	-3.68636	-1.73282	-5.46991
C29	-4.22536	1.786746	-0.77739
C30	-5.62178	2.01606	-0.60937
C31	-6.07992	2.561939	0.617416
C32	-5.18344	2.865133	1.616543
C33	-3.79634	2.674632	1.4195
C34	-3.30432	2.153808	0.235921
H35	-7.14389	2.730506	0.753952
H36	-5.53402	3.276554	2.557699
H37	-3.10266	2.965375	2.202508
C38	-2.00234	-0.75101	1.259219
C39	-2.32505	-1.81031	2.169805
C40	-1.9564	-1.71524	3.53619
C41	-1.28191	-0.61132	3.997843
C42	-0.96402	0.436205	3.109707
C43	-1.31324	0.399026	1.767143
H44	-2.2136	-2.53236	4.204044
H45	-0.99469	-0.53615	5.041709
H46	-0.44221	1.309852	3.489041
H47	-6.59155	0.8315	-3.65966

H48	-7.55074	1.847706	-1.58353
C49	-1.82966	2.114127	-0.04039
C50	-0.90462	1.510631	0.882043
C51	0.414449	1.944373	0.893324
C52	0.871998	2.93818	0.011193
C53	0.018886	3.485346	-0.93451
C54	-1.32392	3.082148	-0.95674
H55	1.120704	1.465098	1.563359
H56	1.909504	3.253495	0.056442
H57	0.364739	4.244967	-1.6281
H58	-2.0344	3.630497	-1.56685
C59	-1.30364	1.950906	-3.96089
H60	-0.257	1.750421	-3.78241
H61	-1.9028	1.232253	-4.49554
H62	-1.77998	2.831311	-3.56316
O63	-0.91852	2.871439	-5.64382
V64	-0.00283	4.22238	-5.71541
Cl65	0.034919	5.011079	-7.70444
Cl66	-0.91422	5.613988	-4.30964
Cl67	1.963863	3.661893	-5.01318

Table S91. [Rh^{III}]
^{II}(bisq)(Me_{eq}...OVCl₃)(TFA_{eq})(TFAH_{ax})]⁺⁺
thermodynamic values

Temp	298.15	498.15
E_{gas}	-3762.62	-3762.62
E_{solv}	-3762.68	-3762.68
G	-3762.30	-3762.38
ZPE	281.533	281.533
H_{vib}	25.525	63.714
S_{trans}	46.093	48.643
S_{rot}	39.129	40.659
S_{vib}	179.449	277.942
solv	-37.0	-37.0

Table S92.
[Rh^{III}(bisq)(CH₂TFA_{ax}...H...TFA_{eq})(TFA_{eq})]⁺⁺
Cartesian coordinates

Atom	x	y	z
Rh1	-2.81907	0.329754	-1.50195
N2	-1.64477	-0.74523	-0.06011
C3	-1.9468	-2.03003	0.111795
C4	-1.20403	-2.90798	0.917622
C5	-0.09452	-2.42458	1.565048
C11	-6.30579	-0.36118	1.840018
C12	-6.49801	-0.89591	0.587456
C13	-5.54176	-0.65494	-0.41879
N14	-4.46964	0.103007	-0.22168
H15	-2.81198	-2.39686	-0.42042
H16	-1.51315	-3.94403	0.987214
H17	0.527941	-3.07185	2.176402
H23	-5.65091	-1.11934	-1.38845
O28	-1.10745	0.749542	-2.6002
C29	-0.53921	-0.22717	-3.16499
O30	-0.9566	-1.40832	-3.18163
C31	0.790073	0.118846	-3.87625
F32	1.416009	-0.97769	-4.29446
F33	0.544879	0.91789	-4.91892
F34	1.591264	0.773153	-3.01119
O35	-4.00146	1.417384	-2.77486
C36	-3.78091	1.398488	-4.06099
O37	-3.05704	0.657326	-4.70021
C38	-4.59832	2.513535	-4.76905
F39	-4.5603	2.37474	-6.09198
F40	-5.88279	2.503059	-4.36925
F41	-4.07509	3.721945	-4.45123
H42	-2.23848	-1.30442	-2.81717
C43	-3.56459	-1.50991	-2.9139
H44	-3.30198	-1.82836	-3.92921
H46	-4.41858	-0.85007	-3.00636
C41	0.245368	-1.05615	1.442161
C42	-0.5765	-0.20595	0.632347
C35	-0.25687	1.185002	0.552623
C44	0.873	1.650089	1.214444
C45	1.698901	0.805476	1.981329
C46	1.383103	-0.52555	2.102785
H50	1.107995	2.708668	1.162743
H51	2.569391	1.216064	2.482403

H52	1.995918	-1.19351	2.700838
C47	-4.30383	0.735564	0.992786
C48	-5.18822	0.476522	2.079712
C49	-4.91724	1.073304	3.338063
C50	-3.83267	1.906356	3.490591
C51	-3.01031	2.219197	2.383705
C52	-3.23804	1.658964	1.139441
H55	-5.58119	0.86642	4.171681
H56	-3.62445	2.361381	4.453724
H57	-2.2071	2.940244	2.504596
H53	-7.0041	-0.5641	2.647047
H54	-7.35192	-1.52378	0.36017
C55	-1.085	2.157432	-0.19122
C56	-2.52152	2.169549	-0.08357
C57	-3.23919	3.169327	-0.82397
C58	-2.59396	4.081483	-1.63602
C59	-1.19454	4.050102	-1.717
C60	-0.45766	3.096784	-1.01571
H63	-4.31805	3.203426	-0.71931
H64	-3.1653	4.806193	-2.20407
H65	-0.67485	4.760934	-2.35291
H66	0.617281	3.045719	-1.15047
O62	-3.95809	-2.6467	-2.12846
C63	-3.7203	-3.88127	-2.63183
O64	-3.21679	-4.14329	-3.68617
C65	-4.2131	-4.9315	-1.61148
F66	-3.55944	-4.7635	-0.43262
F67	-5.52484	-4.7747	-1.37673
F68	-3.98427	-6.15813	-2.05361

Table S93.

$[\text{Rh}^{\text{III}}(\text{bisq})(\text{CH}_2\text{TFA}_{\text{ax}}\cdots\text{H}\cdots\text{TFA}_{\text{eq}})(\text{TFA}_{\text{eq}})]^{+\ddagger}$
thermodynamic values

Temp	298.15	498.15
E _{gas}	-2760.82	-2760.82
E _{solv}	-2760.89	-2760.89
G	-2760.49	-2760.57
ZPE	287.590	287.590
H _{vib}	24.182	62.490

S_{trans}	45.875	48.425
S_{rot}	38.488	40.018
S_{vib}	162.348	260.026
solv	-46.2	-46.2

Table S94.

[Rh^{III}(bisq)(CH₂TFA_{eq}...H...TFA_{ax})(TFA_{eq})]⁺⁺

Cartesian coordinates

Atom	x	y	z
Rh1	-1.33736	0.025765	-1.55983
N2	-1.72188	-1.35782	-0.02888
C3	-1.71596	-2.67194	-0.2129
C4	-2.15433	-3.56516	0.786075
C5	-2.63162	-3.0669	1.977241
C11	-6.18348	0.995219	-1.73517
C12	-5.63003	-0.18057	-2.17803
C13	-4.24381	-0.35792	-2.05348
N14	-3.42167	0.55041	-1.52798
H15	-1.38558	-3.02522	-1.18162
H16	-2.12793	-4.63019	0.585346
H17	-3.00959	-3.73267	2.747859
H22	-3.78806	-1.27491	-2.40245
O27	0.601476	-0.59669	-1.42446
C28	1.331418	-0.73992	-2.4926
O29	1.041207	-0.50717	-3.65311
C30	2.738976	-1.276	-2.11329
F31	3.331172	-0.4357	-1.23747
F32	2.635527	-2.48371	-1.52656
F33	3.517974	-1.38742	-3.18674
H34	-0.24014	1.669398	-4.09085
H35	-1.31146	0.56014	-3.72061
O36	-1.6386	-1.56762	-2.84697
C37	-1.78906	-1.34249	-4.08828
O38	-1.7651	-0.22097	-4.63016
C39	-2.13393	-2.59119	-4.93069
F40	-2.06978	-2.33484	-6.22932
F41	-1.31255	-3.5986	-4.62588
F42	-3.3966	-2.95265	-4.61158
C43	-0.78086	1.663087	-3.13523

H45	-0.03137	1.945536	-2.39797
C41	-5.35693	1.976536	-1.14146
C42	-3.95054	1.724765	-1.0226
C35	-3.13171	2.718501	-0.40084
C44	-3.71864	3.900557	0.027616
C45	-5.09833	4.150978	-0.10571
C46	-5.90577	3.199667	-0.67606
H50	-3.09204	4.650464	0.500646
H51	-5.51063	5.09032	0.247818
H52	-6.973	3.366122	-0.78769
C47	-2.10152	-0.83257	1.179999
C48	-2.61895	-1.66876	2.210373
C49	-3.07791	-1.06249	3.407952
C50	-2.99473	0.302422	3.568015
C51	-2.40995	1.109513	2.564683
C52	-1.95331	0.558986	1.380298
H55	-3.48677	-1.69029	4.19396
H56	-3.34585	0.766678	4.484019
H57	-2.28757	2.173947	2.742257
H53	-7.24839	1.187155	-1.82997
H54	-6.22616	-0.9643	-2.63116
C55	-1.67429	2.553348	-0.19847
C56	-1.13387	1.377446	0.41752
C57	0.284893	1.29816	0.592864
C58	1.121182	2.32683	0.200891
C59	0.564766	3.491396	-0.34905
C60	-0.80857	3.596391	-0.55742
H63	0.69578	0.415848	1.070437
H64	2.194102	2.237085	0.334947
H65	1.21215	4.315988	-0.6347
H66	-1.21796	4.473573	-1.04574
O62	-1.82945	2.650814	-3.16368
C63	-1.86246	3.508822	-4.19821
O64	-1.10686	3.557414	-5.12965
C65	-3.04038	4.485415	-3.98713
F66	-4.18719	3.813754	-3.7704
F67	-2.79899	5.250065	-2.89483
F68	-3.19144	5.279532	-5.03775

Table S95.

$[\text{Rh}^{\text{III}}(\text{bisq})(\text{CH}_2\text{TFA}_{\text{eq}}\cdots\text{H}\cdots\text{TFA}_{\text{ax}})(\text{TFA}_{\text{eq}})]^{+\ddagger}$
thermodynamic values

Temp	298.15	498.15
E _{gas}	-2760.83	-2760.83
E _{solv}	-2760.90	-2760.90
G	-2760.50	-2760.58
ZPE	287.780	287.780
H _{vib}	24.689	63.319
S _{trans}	45.875	48.425
S _{rot}	38.436	39.966
S _{vib}	162.711	260.198
solv	-45.7	-45.7

Table S96.

$[\text{Rh}^{\text{III}}(\text{bisq})(\text{CH}_2\text{TFA}_{\text{eq}}\cdots\text{H}\cdots\text{TFA}_{\text{eq}})(\text{TFA}_{\text{ax}})]^{+\ddagger}$
Cartesian coordinates

Atom	x	y	z
Rh1	-2.73403	0.179693	-1.33666
N2	-1.6613	-0.97498	0.078617
C3	-2.02111	-2.23648	0.293919
C4	-1.31822	-3.09151	1.161357
C5	-0.20178	-2.61713	1.805446
C11	-6.01655	0.153741	2.246386
C12	-6.27804	-0.52205	1.0767
C13	-5.3677	-0.42614	0.005975
N14	-4.27909	0.334661	0.072485
H15	-2.87406	-2.59351	-0.26789
H16	-1.66341	-4.11133	1.286928
H17	0.376698	-3.25395	2.468663
H23	-5.49902	-1.00053	-0.90309
O28	-1.12034	-0.23128	-2.57213
C29	-1.11776	0.337322	-3.7064
O30	-1.97551	1.141366	-4.12383
C31	0.126132	0.058513	-4.57896
F32	1.120094	0.868276	-4.14165
F33	0.52668	-1.20812	-4.45193
F34	-0.10904	0.325232	-5.85877

H35	-4.1	2.246965	-3.46563
H36	-2.97668	1.136825	-3.22817
O37	-3.60802	-1.53882	-1.90083
C38	-3.62655	-2.03203	-3.11781
O39	-3.24176	-1.54651	-4.15592
C40	-4.24371	-3.46037	-3.05143
F41	-4.38623	-3.98188	-4.26201
F42	-3.42825	-4.25891	-2.32363
F43	-5.44277	-3.43773	-2.43587
C44	-4.2107	1.42087	-2.74812
H46	-4.58247	1.857587	-1.82916
C41	-4.0265	1.088711	1.196183
C42	-4.87024	0.982607	2.341087
C43	-4.53556	1.715925	3.508301
C36	-3.42713	2.531356	3.520698
C45	-2.63693	2.679346	2.35775
C46	-2.92288	1.97919	1.199072
H49	-5.17174	1.628624	4.384103
H50	-3.17066	3.092535	4.413522
H51	-1.80495	3.377621	2.364894
C48	-0.55652	-0.45471	0.717137
C49	0.2145	-1.28085	1.594679
C50	1.379105	-0.75472	2.209551
C51	1.772161	0.537852	1.959503
C52	1.006243	1.349902	1.097327
C53	-0.14929	0.886658	0.486509
H55	1.956555	-1.39615	2.868571
H56	2.667809	0.941922	2.420051
H57	1.322117	2.372742	0.913814
H53	-7.154	-1.15101	0.965371
H54	-6.68175	0.065834	3.10094
C55	-0.89639	1.826703	-0.39638
C56	-2.20079	2.303809	-0.07979
C57	-2.71322	3.409758	-0.81986
C58	-1.98967	4.000027	-1.8366
C59	-0.71308	3.505511	-2.16062
C60	-0.18077	2.443309	-1.45431
H63	-3.68035	3.813846	-0.53521
H64	-2.39799	4.851056	-2.37305
H65	-0.14112	3.961567	-2.96289

H66	0.802864	2.061342	-1.70539
O62	-5.20691	0.513684	-3.21844
C63	-5.49361	0.559463	-4.53874
O64	-5.02734	1.319303	-5.34135
C65	-6.59585	-0.46928	-4.86868
F66	-6.43858	-1.60454	-4.16041
F67	-7.7918	0.056629	-4.5458
F68	-6.58274	-0.75984	-6.16395

Table S97.

$[\text{Rh}^{\text{III}}(\text{bisq})(\text{CH}_2\text{TFA}_{\text{eq}}\cdots\text{H}\cdots\text{TFA}_{\text{eq}})(\text{TFA}_{\text{ax}})]^{+\ddagger}$
thermodynamic values

Temp	298.15	498.15
E_{gas}	-2760.83	-2760.83
E_{solv}	-2760.90	-2760.90
G	-2760.50	-2760.58
ZPE	287.770	287.770
H_{vib}	24.045	62.288
S_{trans}	45.875	48.425
S_{rot}	38.397	39.927
S_{vib}	161.252	258.763
solv	-45.5	-45.5

Rh(bisq^{F2}) complexes

Table S98. Rh^I(bisq^{F2})(TFA)(TFAH) Cartesian coordinates

Atom	x	y	z
Rh1	-1.11714	0.440018	-1.5427
N2	-1.6097	-0.89959	-0.05927
C3	-1.7867	-2.16715	-0.43266
C4	-2.5104	-3.10075	0.332922
C5	-3.09274	-2.68996	1.508841
C6	-5.48968	2.589173	-1.57281
C7	-5.21355	1.364107	-2.12512
C8	-3.92639	0.824869	-1.95453
N9	-2.94938	1.425903	-1.27541
H10	-1.35668	-2.43645	-1.39023

H11	-2.62387	-4.11442	-0.0362
H12	-3.70219	-3.36597	2.102188
H13	-3.665	-0.12611	-2.40301
O14	0.527987	-0.83379	-1.93069
C15	1.746359	-0.66414	-2.08766
O16	2.392816	0.405147	-2.3415
C17	2.612709	-1.93968	-1.98799
F18	3.920968	-1.67007	-1.95475
F19	2.293004	-2.62841	-0.87622
F20	2.368681	-2.73236	-3.05068
O21	-0.89727	1.826471	-3.1333
C22	0.087379	2.548724	-3.40536
O23	1.299252	2.424008	-3.08989
C24	-0.2411	3.839037	-4.19568
F25	-0.43526	4.852621	-3.3132
F26	0.755101	4.197392	-5.01736
F27	-1.36103	3.715347	-4.92443
H28	1.786194	1.30364	-2.60582
C29	-3.20297	2.64406	-0.67664
C30	-4.48874	3.264002	-0.83475
C31	-4.7466	4.538425	-0.26903
C32	-3.76814	5.191405	0.435951
C33	-2.51196	4.577103	0.613344
C34	-2.2048	3.328321	0.092366
H35	-5.72793	4.982169	-0.41202
H36	-3.9534	6.170565	0.867032
H37	-1.75053	5.090126	1.193114
C39	-2.05992	-0.49617	1.182115
C40	-2.87782	-1.36707	1.969987
C41	-3.42864	-0.89616	3.189557
C42	-3.14627	0.373069	3.632787
C43	-2.25911	1.193919	2.901888
C44	-1.69973	0.785283	1.702897
H45	-4.0649	-1.56152	3.766748
H46	-3.56702	0.736761	4.565473
H47	-1.975	2.161754	3.304347
H49	-5.95001	0.812378	-2.6989
H50	-6.46289	3.05739	-1.69223
C51	-0.83697	2.805184	0.373856
C52	-0.60668	1.619434	1.10345

C53	0.709496	1.2667	1.43778
C54	1.777159	2.048532	1.025874
C55	1.551756	3.209889	0.295264
C56	0.257319	3.591003	-0.02059
H59	0.913785	0.374576	2.020197
F56	3.034942	1.697853	1.339236
F57	2.595581	3.955065	-0.09592
H62	0.111546	4.481965	-0.6215

Table S99. Rh^I(bisq^{F2})(TFA)(TFAH)
thermodynamic values

Temp	298.15	498.15
E_{gas}	-2394.15	-2394.15
E_{solv}	-2394.18	-2394.18
G	-2393.84	-2393.91
ZPE	241.405	241.405
H_{vib}	20.677	53.426
S_{trans}	45.510	48.060
S_{rot}	37.861	39.391
S_{vib}	140.077	223.723
solv	-14.7	-14.7

Table S100. Rh^I(bisq^{F2})(κ¹-TFA) Cartesian
coordinates

Atom	x	y	z
Rh1	-1.37754	0.531984	-1.98544
N2	-2.37908	-0.73138	-0.38585
C3	-3.27898	-1.6358	-0.73951
C4	-4.04001	-2.3889	0.176595
C5	-3.82105	-2.19085	1.515863
C6	-5.50274	3.091193	-1.9216
C7	-5.31331	2.148938	-2.90824
C8	-4.10234	1.426657	-2.95905
N9	-3.11111	1.632968	-2.09995
H10	-3.40608	-1.79401	-1.80627
H11	-4.76182	-3.11241	-0.18754
H12	-4.37065	-2.75418	2.265583
H13	-3.93625	0.657242	-3.70745

O14	0.300002	-0.58581	-2.22104
C15	0.742895	-1.52918	-1.45766
O16	0.305403	-1.95666	-0.3993
C17	2.065434	-2.11531	-2.02148
F18	2.444632	-3.21541	-1.35194
F19	1.955484	-2.44681	-3.32533
F20	3.060091	-1.20526	-1.9121
C21	-4.46705	3.337642	-0.98455
C22	-3.26244	2.59468	-1.12761
C23	-2.16259	2.788308	-0.26062
C24	-2.29642	3.691963	0.777309
C25	-3.49773	4.418725	0.954998
C26	-4.55851	4.259898	0.089475
H27	-1.46403	3.851913	1.456159
H28	-3.57491	5.119521	1.781253
H29	-5.47409	4.829653	0.221489
C30	-2.85262	-1.24805	1.941493
C31	-2.13308	-0.50023	0.94974
C32	-1.13704	0.446077	1.401109
C33	-0.91776	0.573222	2.763624
C34	-1.63317	-0.1662	3.727584
C35	-2.59388	-1.05765	3.323024
H36	-0.16233	1.279862	3.094719
H37	-1.42286	-0.01986	4.78303
H38	-3.16472	-1.63565	4.04502
H39	-6.08369	1.937632	-3.64199
H40	-6.43435	3.645676	-1.84967
C41	-0.88737	2.048259	-0.55587
C42	-0.28334	1.223184	0.468062
C43	1.08991	1.045569	0.475285
C44	1.898789	1.631254	-0.51151
C45	1.339235	2.358398	-1.54152
C46	-0.04794	2.570355	-1.60593
H47	1.556381	0.370608	1.184839
F48	3.230699	1.447506	-0.46831
F49	2.129037	2.887861	-2.49107
H50	-0.41989	3.33391	-2.28026

Table S101. Rh^I(bisq^{F2})(κ¹-TFA) thermodynamic
values

Temp	298.15	498.15
E _{gas}	-1867.35	-1867.35
E _{solv}	-1867.38	-1867.38
G	-1867.07	-1867.13
ZPE	216.879	216.879
H _{vib}	16.533	43.909
S _{trans}	44.978	47.529
S _{rot}	36.815	38.345
S _{vib}	106.290	175.309
solv	-19.3	-19.3

Table S102. Rh^I(bisq^{F2})(κ²-TFA) Cartesian coordinates

Atom	x	y	z
Rh1	-1.42208	0.484297	-2.06135
N2	-2.18818	-0.72805	-0.56989
C3	-2.9322	-1.75954	-0.96947
C4	-3.66312	-2.58097	-0.09083
C5	-3.61928	-2.31556	1.255738
C6	-5.52652	3.059596	-1.57054
C7	-5.37066	2.067555	-2.50689
C8	-4.12716	1.416409	-2.60498
N9	-3.07728	1.705035	-1.83525
H10	-2.94948	-1.93447	-2.03882
H11	-4.24974	-3.39949	-0.49398
H12	-4.17865	-2.91547	1.968446
H13	-3.96798	0.629566	-3.33274
O14	-0.30117	1.361293	-3.70258
C15	0.556942	0.446469	-3.54763
O16	0.386475	-0.50786	-2.73635
C17	1.891567	0.549145	-4.30114
F18	2.772613	1.260105	-3.56101
F19	2.424724	-0.66186	-4.52776
F20	1.744888	1.173472	-5.48053
C21	-4.43197	3.419872	-0.74729
C22	-3.18757	2.723849	-0.9068
C23	-2.06421	3.125695	-0.11609
C24	-2.23005	4.15978	0.791638
C25	-3.46232	4.823437	0.969075

C26	-4.54609	4.460856	0.208862
H27	-1.37129	4.469562	1.37967
H28	-3.54148	5.624236	1.698306
H29	-5.50138	4.967713	0.315827
C30	-2.81723	-1.24931	1.731334
C31	-2.07967	-0.46504	0.783251
C32	-1.21008	0.56485	1.263236
C33	-1.14226	0.789726	2.629123
C34	-1.89956	0.044935	3.558417
C35	-2.72015	-0.96354	3.1172
H36	-0.46975	1.56208	2.990488
H37	-1.81516	0.264972	4.61855
H38	-3.29557	-1.56485	3.815768
H39	-6.17828	1.772069	-3.16798
H40	-6.47102	3.584094	-1.45408
C41	-0.68605	2.555088	-0.25656
C42	-0.28725	1.358923	0.38789
C43	1.062117	0.980372	0.355627
C44	1.988578	1.737687	-0.34749
C45	1.596642	2.910845	-0.98117
C46	0.276386	3.332883	-0.91438
H47	1.397011	0.073857	0.847826
F48	3.275134	1.357076	-0.39923
F49	2.510292	3.644351	-1.63656
H50	-0.00099	4.254854	-1.4132

Table S103. Rh^I(bisq^{F2})(κ²-TFA) thermodynamic values

Temp	298.15	498.15
E _{gas}	-1867.36	-1867.36
E _{solv}	-1867.39	-1867.39
G	-1867.08	-1867.14
ZPE	217.304	217.304
H _{vib}	16.506	43.818
S _{trans}	44.978	47.529
S _{rot}	36.889	38.419
S _{vib}	105.975	174.831
solv	-16.4	-16.4

Table S104. Rh^I(bisq^{F2})(Me) Cartesian coordinates

Atom	x	y	z
Rh1	-1.07319	0.828674	-1.8374
N2	-2.32744	-0.28066	-0.37585
C3	-3.38614	-1.01776	-0.68261
C4	-4.08762	-1.79533	0.262674
C5	-3.6587	-1.8007	1.569877
C6	-5.52697	2.958565	-2.05775
C7	-5.15566	2.305783	-3.20853
C8	-3.83394	1.816442	-3.3186
N9	-2.91766	1.969401	-2.37379
H10	-3.69844	-0.9941	-1.72338
H11	-4.94749	-2.37671	-0.05433
H12	-4.16812	-2.39418	2.324849
H13	-3.51722	1.28001	-4.20895
C22	-4.57783	3.150637	-1.02013
C23	-3.25188	2.662624	-1.22556
C24	-2.25587	2.85823	-0.21578
C25	-2.62586	3.482407	0.961793
C26	-3.94949	3.930289	1.183984
C27	-4.90564	3.783827	0.207277
H28	-1.87405	3.640813	1.729422
H29	-4.20062	4.407573	2.127084
H30	-5.92085	4.141146	0.360245
C31	-2.53119	-1.02483	1.940831
C32	-1.89131	-0.25349	0.923873
C33	-0.75147	0.5492	1.22363
C34	-0.27438	0.527627	2.526366
C35	-0.89146	-0.24625	3.535858
C36	-2.00596	-1.00323	3.258202
H37	0.588489	1.136616	2.778631
H38	-0.4817	-0.22999	4.541943
H39	-2.48857	-1.59643	4.030499
H40	-5.85481	2.149678	-4.02394
H41	-6.53999	3.328704	-1.92471
C42	-0.81448	2.485219	-0.49215
C43	-0.09284	1.39223	0.177256
C44	1.337265	1.438719	0.201363

C45	2.029925	2.485677	-0.34815
C46	1.338773	3.579918	-0.90932
C47	-0.02723	3.60014	-0.96266
H48	1.891957	0.631446	0.669108
F41	3.38014	2.506132	-0.34373
F42	2.060881	4.61637	-1.37862
H51	-0.52089	4.468449	-1.38526
C52	0.143797	1.533243	-3.31898
H53	1.157603	1.753704	-2.96382
H54	0.189769	0.696228	-4.03984
H55	-0.2414	2.417512	-3.84145

Table S105. Rh^I(bisq^{F2})(Me) thermodynamic values

Temp	298.15	498.15
E _{gas}	-1381.03	-1381.03
E _{solv}	-1381.05	-1381.05
G	-1380.73	-1380.78
ZPE	220.857	220.857
H _{vib}	13.534	37.442
S _{trans}	44.431	46.981
S _{rot}	35.830	37.360
S _{vib}	84.290	144.491
solv	-11.3	-11.3

Table S106. Rh^I(bisq^{F2})(Me)(TFAH) Cartesian coordinates

Atom	x	y	z
Rh1	-1.29901	0.544921	-2.29349
N2	-2.18596	-0.32275	-0.34082
C3	-3.15074	-1.16761	-0.68672
C4	-3.82141	-2.02003	0.212989
C5	-3.4516	-1.99403	1.533798
C6	-5.34501	3.070533	-2.06078
C7	-4.9024	2.486145	-3.22225
C8	-3.58997	1.98137	-3.2814
N9	-2.7227	2.040544	-2.26289
H10	-3.39922	-1.18279	-1.74402

H11	-4.59932	-2.68205	-0.15259
H12	-3.92486	-2.64206	2.267049
H13	-3.23193	1.489225	-4.17516
O14	-0.1601	-1.27938	-2.44486
C15	1.059856	-1.14482	-2.47668
O16	1.688573	-0.00306	-2.36948
C17	1.995361	-2.34853	-2.64744
F18	2.704246	-2.22635	-3.78151
F19	2.855207	-2.41726	-1.61546
F20	1.297916	-3.48643	-2.69785
H21	0.941622	0.684193	-2.3021
C22	-4.45108	3.19808	-0.96796
C23	-3.11246	2.708074	-1.11356
C24	-2.18722	2.911345	-0.04694
C25	-2.63014	3.50261	1.12573
C26	-3.96392	3.930268	1.29029
C27	-4.85423	3.797634	0.252356
H28	-1.91685	3.661112	1.929024
H29	-4.27105	4.38667	2.226766
H30	-5.87819	4.150243	0.345432
C31	-2.42878	-1.11041	1.956692
C32	-1.81276	-0.25328	0.981736
C33	-0.7873	0.65146	1.422849
C34	-0.41466	0.628076	2.760023
C35	-1.01214	-0.22933	3.706144
C36	-2.01316	-1.08059	3.311951
H37	0.358223	1.316292	3.08932
H38	-0.68285	-0.20047	4.740642
H39	-2.49905	-1.74423	4.022374
H40	-5.54495	2.384838	-4.0908
H41	-6.36059	3.444586	-1.96375
C42	-0.72072	2.642306	-0.1756
C43	-0.0673	1.620185	0.545909
C44	1.336794	1.571923	0.535542
C45	2.074989	2.505249	-0.1747
C46	1.427187	3.513151	-0.88231
C47	0.044652	3.589771	-0.87202
H48	1.869052	0.791009	1.067977
F49	3.417621	2.450144	-0.1807
F50	2.155487	4.420311	-1.55428

H51	-0.43522	4.396933	-1.41446
C52	-0.54875	1.151954	-4.12776
H53	0.241097	1.915562	-4.0485
H54	-0.13272	0.304137	-4.69224
H55	-1.33518	1.596058	-4.75463

Table S107. Rh^I(bisq^{F2})(Me)(TFAH)
thermodynamic values

Temp	298.15	498.15
E _{gas}	-1907.82	-1907.82
E _{solv}	-1907.83	-1907.83
G	-1907.48	-1907.55
ZPE	246.715	246.715
H _{vib}	18.331	48.065
S _{trans}	45.059	47.609
S _{rot}	37.153	38.683
S _{vib}	119.603	194.580
solv	-11.3	-11.3

Table S108. Rh^{II}(bisq^{F2})(TFA)₂ Cartesian
coordinates

Atom	x	y	z
Rh1	-0.86094	0.725226	-1.90881
N2	-1.66081	-0.74265	-0.62064
C3	-2.13823	-1.86324	-1.15305
C4	-2.93998	-2.76815	-0.42637
C5	-3.26173	-2.47949	0.877427
C6	-5.23845	2.923928	-1.84651
C7	-4.95436	1.864571	-2.67268
C8	-3.66566	1.29814	-2.63262
N9	-2.71026	1.728955	-1.81523
H10	-1.855	-2.04495	-2.18605
H11	-3.29811	-3.66659	-0.91701
H12	-3.89868	-3.14089	1.458715
H13	-3.38486	0.498136	-3.30818
O14	0.967049	-0.22171	-2.06207
C15	0.946382	-1.27799	-2.79457
O16	-0.02039	-1.8167	-3.33085

C17	2.352457	-1.91204	-2.94263
F18	2.756412	-2.42016	-1.75355
F19	2.35266	-2.91329	-3.83388
F20	3.267564	-1.00611	-3.33308
O21	-0.15705	2.151344	-3.24386
C22	-0.6534	1.895739	-4.40064
O23	-1.45372	1.003416	-4.6864
C24	-0.1566	2.869378	-5.49595
F25	-0.69174	2.585701	-6.69158
F26	-0.49843	4.141102	-5.18317
F27	1.183342	2.822695	-5.61549
C29	-4.23838	3.427173	-0.9786
C30	-2.95535	2.791607	-0.97541
C31	-1.92806	3.296073	-0.12033
C32	-2.20564	4.403972	0.66327
C33	-3.47032	5.030796	0.662343
C34	-4.47359	4.546452	-0.14054
H35	-1.41862	4.797551	1.2999
H36	-3.64014	5.894842	1.2974
H37	-5.45328	5.015765	-0.1583
C38	-2.74552	-1.30779	1.486085
C39	-1.90348	-0.45712	0.703959
C40	-1.29983	0.685592	1.307093
C41	-1.59876	0.972076	2.627619
C42	-2.47234	0.163364	3.388666
C43	-3.02583	-0.9659	2.833701
H44	-1.12826	1.832533	3.09425
H45	-2.68184	0.428062	4.420594
H46	-3.67411	-1.615	3.415668
H47	-5.68831	1.46349	-3.36278
H48	-6.21707	3.396336	-1.85452
C49	-0.54711	2.72298	-0.0607
C50	-0.25731	1.500397	0.597583
C51	1.086456	1.108479	0.756839
C52	2.108377	1.889246	0.255112
C53	1.821812	3.092616	-0.39271
C54	0.514831	3.513435	-0.53951
H55	1.337298	0.179842	1.256853
F56	3.383609	1.510934	0.392085
F57	2.831158	3.832475	-0.86511

H58	0.320392	4.441539	-1.06391
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Table S109. Rh^{II}(bisq^{F2})(TFA)₂ thermodynamic values

Temp	298.15	498.15
E_{gas}	-2393.55	-2393.55
E_{solv}	-2393.58	-2393.58
G	-2393.26	-2393.33
ZPE	236.072	236.072
H_{vib}	19.962	51.979
S_{trans}	45.506	48.056
S_{rot}	37.823	39.353
S_{vib}	138.627	221.441
solv	-22.0	-22.0

Table S110. [Rh^{II}(bisq^{F2})(TFA)(TFAH)]⁺ Cartesian coordinates

Atom	x	y	z
Rh1	-1.10932	0.556334	-1.46324
N2	-1.76926	-0.87167	-0.11245
C3	-2.05121	-2.10018	-0.5328
C4	-2.72696	-3.03857	0.269615
C5	-3.14271	-2.6604	1.526389
C6	-5.54506	2.519221	-1.67904
C7	-5.1965	1.357369	-2.32619
C8	-3.89284	0.865399	-2.15798
N9	-2.97681	1.458989	-1.39608
H10	-1.74035	-2.34818	-1.54322
H11	-2.92581	-4.02909	-0.12353
H12	-3.69852	-3.34716	2.157632
H13	-3.58153	-0.04026	-2.66985
O14	0.54798	-0.74399	-1.71394
C15	1.769288	-0.70552	-1.9557
O16	2.491741	0.291011	-2.27383
C17	2.509142	-2.06203	-1.85882
F18	3.817862	-1.93213	-2.04609
F19	2.28767	-2.59381	-0.6447
F20	2.008173	-2.89314	-2.78655

O21	-0.76727	1.937268	-2.98484
C22	0.276359	2.591419	-3.28021
O23	1.459014	2.393562	-2.94065
C24	-0.01296	3.858195	-4.12604
F25	-0.53829	4.797994	-3.30128
F26	1.091676	4.352116	-4.67884
F27	-0.90823	3.601861	-5.08816
H28	1.957807	1.20629	-2.49331
C29	-3.28652	2.624377	-0.72941
C30	-4.59738	3.187487	-0.86842
C31	-4.91427	4.407782	-0.21782
C32	-3.96562	5.058952	0.531308
C33	-2.67518	4.504747	0.664002
C34	-2.3177	3.305546	0.06755
H35	-5.91259	4.81843	-0.33566
H36	-4.1981	5.997895	1.023093
H37	-1.93493	5.028246	1.261775
C38	-2.08616	-0.49161	1.170065
C39	-2.83389	-1.36677	2.015094
C40	-3.21987	-0.91606	3.30402
C41	-2.85326	0.338085	3.733529
C42	-2.04978	1.167062	2.916607
C43	-1.65022	0.772568	1.651733
H44	-3.79619	-1.57813	3.943108
H45	-3.14583	0.686606	4.718804
H46	-1.70806	2.12214	3.304514
H47	-5.89093	0.823249	-2.96427
H48	-6.53933	2.942844	-1.78776
C49	-0.92348	2.816235	0.257761
C50	-0.6273	1.585271	0.905481
C51	0.728996	1.243022	1.130951
C52	1.745697	2.08833	0.736014
C53	1.445613	3.309825	0.119022
C54	0.131392	3.666083	-0.12329
H55	0.986395	0.326667	1.651762
F56	3.021404	1.761543	0.943958
F57	2.442594	4.107295	-0.24768
H58	-0.06683	4.595259	-0.64576

Table S111. $[\text{Rh}^{\text{II}}(\text{bisq}^{\text{F2}})(\text{TFA})(\text{TFAH})]^+$
thermodynamic values

Temp	298.15	498.15
E_{gas}	-2393.93	-2393.93
E_{solv}	-2394.00	-2394.00
G	-2393.66	-2393.73
ZPE	243.102	243.102
H_{vib}	20.470	53.013
S_{trans}	45.510	48.060
S_{rot}	37.820	39.351
S_{vib}	138.505	221.626
solv	-44.5	-44.5

Table S112. $\text{Rh}^{\text{III}}(\text{bisq}^{\text{F2}})(\text{Me}_{\text{ax}})(\text{H}_{\text{eq}})(\text{TFA}_{\text{eq}})$
Cartesian coordinates

Atom	x	y	z
Rh1	-1.60695	0.144044	-1.99856
N2	-2.28321	-1.02724	0.138293
C3	-3.01449	-2.10277	-0.09917
C4	-3.45728	-3.0002	0.897265
C5	-3.10116	-2.7586	2.199623
C6	-6.20428	1.762413	-1.91983
C7	-5.72126	1.153574	-3.05298
C8	-4.36777	0.762824	-3.09705
N9	-3.51544	0.984883	-2.10263
H10	-3.26467	-2.28971	-1.13826
H11	-4.05479	-3.86158	0.61709
H12	-3.40606	-3.42572	3.002015
H13	-3.97091	0.229954	-3.95251
O14	0.234322	-0.71252	-1.74111
C15	1.272834	-0.33829	-2.4088
O16	1.392487	0.502043	-3.28792
C17	2.540597	-1.07528	-1.89647
F18	3.585333	-0.90952	-2.71952
F19	2.897898	-0.58165	-0.68062
F20	2.343011	-2.40137	-1.74642
H21	-1.19331	0.801417	-3.30676
C22	-3.94416	1.693606	-0.99883

C23	-5.31979	2.04861	-0.84946
C24	-5.7508	2.671983	0.349011
C25	-4.84484	2.954632	1.343377
C26	-3.47324	2.674714	1.156763
C27	-3.00055	2.069618	0.00471
H28	-6.802	2.922712	0.461497
H29	-5.17155	3.42835	2.264225
H30	-2.76278	2.96893	1.922344
C31	-1.92395	-0.75515	1.434361
C32	-2.31244	-1.62272	2.507952
C33	-1.90001	-1.34758	3.836471
C34	-1.1155	-0.25215	4.102315
C35	-0.7317	0.608255	3.05195
C36	-1.12195	0.39365	1.739848
H37	-2.20958	-2.02158	4.630982
H38	-0.79036	-0.03948	5.116382
H39	-0.11711	1.475628	3.275205
H40	-6.36177	0.938896	-3.90167
H41	-7.25175	2.03762	-1.8316
C42	-1.52534	1.958544	-0.22753
C43	-0.64191	1.317239	0.681753
C44	0.735925	1.521415	0.560138
C45	1.250227	2.336034	-0.43977
C46	0.400966	2.933513	-1.36125
C47	-0.97263	2.742144	-1.26576
H48	1.43206	0.998061	1.204818
F49	2.569764	2.525435	-0.541
F50	0.903607	3.706221	-2.32826
H51	-1.61401	3.2788	-1.95542
C52	-2.05849	-1.43601	-3.22414
H53	-1.8075	-1.2223	-4.26675
H54	-1.45142	-2.27592	-2.87539
H55	-3.12467	-1.68834	-3.15678

Table S113. Rh^{III}(bisq^{F2})(Me_{ax})(H_{eq})(TFA_{eq})
thermodynamic values

Temp	298.15	498.15
E _{gas}	-1907.84	-1907.84
E _{solv}	-1907.87	-1907.87

G	-1907.52	-1907.58
ZPE	246.382	246.382
H_{vib}	18.088	47.780
S_{trans}	45.059	47.609
S_{rot}	36.996	38.526
S_{vib}	117.046	191.904
solv	-18.3	-18.3

Table S114. Rh^{III}(bisq^{F2})(Me_{eq})(H_{ax})(TFA_{eq})
Cartesian coordinates

Atom	x	y	z
Rh1	-1.45381	0.440947	-2.02303
N2	-1.96193	-0.93768	-0.12021
C3	-2.46791	-2.10057	-0.50559
C4	-2.90383	-3.10491	0.385641
C5	-2.78526	-2.88733	1.734579
C6	-6.1857	1.558232	-1.79847
C7	-5.65513	0.962126	-2.91626
C8	-4.26453	0.747352	-2.98109
N9	-3.42231	1.114251	-2.01883
H10	-2.51238	-2.26562	-1.57534
H11	-3.31065	-4.02898	-0.01117
H12	-3.1032	-3.63389	2.458064
H13	-1.79691	-0.67578	-2.98356
H14	-3.81903	0.239186	-3.82773
O15	0.492808	-0.19714	-1.96329
C16	0.775779	-1.4466	-2.09091
O17	0.049808	-2.40427	-2.33024
C18	2.291337	-1.68638	-1.8561
F19	2.629942	-2.97252	-2.03343
F20	3.050124	-0.943	-2.6876
F21	2.630256	-1.34863	-0.58648
C22	-3.91479	1.788132	-0.91894
C23	-5.32234	1.988454	-0.76009
C24	-5.81435	2.603111	0.419049
C25	-4.94349	3.018053	1.397213
C26	-3.55197	2.868191	1.212981
C27	-3.01902	2.278365	0.079258
H28	-6.88677	2.737966	0.530093

H29	-5.31584	3.484261	2.304406
H30	-2.87324	3.244419	1.971746
C31	-1.80495	-0.70637	1.224304
C32	-2.21243	-1.6767	2.196908
C33	-2.01143	-1.42941	3.578543
C34	-1.3985	-0.27275	3.993628
C35	-0.97624	0.677925	3.039494
C36	-1.17726	0.496255	1.68175
H37	-2.33502	-2.1791	4.295473
H38	-1.23027	-0.08559	5.049956
H39	-0.48057	1.584459	3.375401
H40	-6.28066	0.630306	-3.73789
H41	-7.25661	1.71038	-1.6952
C42	-1.52919	2.277669	-0.09807
C43	-0.6657	1.521416	0.731637
C44	0.71656	1.739357	0.673172
C45	1.24501	2.678438	-0.19768
C46	0.404944	3.411769	-1.02868
C47	-0.96691	3.21955	-0.98086
H48	1.396968	1.140952	1.268304
F49	2.566564	2.877885	-0.26037
F50	0.931711	4.302256	-1.88274
H51	-1.59834	3.824162	-1.62248
C52	-0.99545	1.427756	-3.76733
H53	-0.62981	0.720421	-4.51646
H54	-1.86154	1.966809	-4.17074
H55	-0.1941	2.139641	-3.54419

Table S115. Rh^{III}(bisq^{F2})(Me_{eq})(H_{ax})(TFA_{eq})
thermodynamic values

Temp	298.15	498.15
E _{gas}	-1907.84	-1907.84
E _{solv}	-1907.87	-1907.87
G	-1907.52	-1907.58
ZPE	246.195	246.195
H _{vib}	17.682	46.998
S _{trans}	45.059	47.609
S _{rot}	37.016	38.546
S _{vib}	118.268	193.178

solv	-16.8	-16.8
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Table S116. Rh^{III}(bisq^{F2})(Me_{eq})(H_{eq})(TFA_{ax})
Cartesian coordinates

Atom	x	y	z
Rh1	-1.47335	0.336814	-1.98896
N2	-2.25669	-1.0897	-0.42476
C3	-2.96322	-2.16968	-0.71241
C4	-3.39618	-3.08307	0.275414
C5	-3.0664	-2.85302	1.589485
C6	-6.36306	1.574501	-1.65762
C7	-5.92357	0.897581	-2.77042
C8	-4.53541	0.677836	-2.93955
N9	-3.63417	1.128535	-2.08622
H10	-3.17696	-2.32767	-1.76537
H11	-3.97312	-3.95312	-0.01995
H12	-3.37603	-3.53855	2.373711
O13	-2.10375	-1.00459	-3.37951
H14	-4.14782	0.089178	-3.76693
H15	-0.06855	-0.28137	-1.9753
C16	-1.36208	-1.81347	-4.07092
O17	-0.15777	-1.97044	-4.10015
C18	-2.28422	-2.71205	-4.94271
F19	-1.59037	-3.51186	-5.75813
F20	-3.0545	-3.50347	-4.14772
F21	-3.1282	-1.97508	-5.70126
C22	-4.03973	1.835248	-0.98935
C23	-5.42106	2.063664	-0.71494
C24	-5.7835	2.755562	0.468482
C25	-4.80957	3.207331	1.329156
C26	-3.44066	3.009163	1.032317
C27	-3.04129	2.335584	-0.1076
H28	-6.83609	2.923157	0.68145
H29	-5.08568	3.735379	2.237052
H30	-2.6875	3.404668	1.707732
C31	-1.91232	-0.83464	0.872356
C32	-2.29716	-1.71126	1.93122
C33	-1.88057	-1.42389	3.255562
C34	-1.10255	-0.31815	3.507036

C35	-0.7223	0.544166	2.453225
C36	-1.11996	0.315061	1.146548
H37	-2.17324	-2.09472	4.058937
H38	-0.77276	-0.09929	4.518287
H39	-0.10762	1.41237	2.674086
H40	-6.61853	0.511927	-3.50912
H41	-7.42358	1.73975	-1.48453
C42	-1.58027	2.256004	-0.4672
C43	-0.68732	1.276407	0.074215
C44	0.721398	1.513093	-0.02835
C45	1.204916	2.651331	-0.61483
C46	0.320758	3.622416	-1.12467
C47	-1.03475	3.432968	-1.05434
H48	1.418856	0.78908	0.377644
F49	2.523453	2.874474	-0.70912
F50	0.834303	4.735386	-1.66592
H51	-1.69356	4.20315	-1.4394
C52	-0.68415	1.475525	-3.52089
H53	-0.44606	0.810081	-4.35239
H54	-1.42758	2.215818	-3.8374
H55	0.230834	1.986247	-3.20847

Table S117. Rh^{III}(bisq^{F2})(Me_{eq})(H_{eq})(TFA_{ax}) thermodynamic values

Temp	298.15	498.15
E_{gas}	-1907.83	-1907.83
E_{solv}	-1907.86	-1907.86
G	-1907.51	-1907.57
ZPE	246.270	246.270
H_{vib}	18.065	47.765
S_{trans}	45.059	47.609
S_{rot}	37.170	38.700
S_{vib}	116.202	191.080
solv	-16.4	-16.4

Table S118. Rh^{III}(bisq^{F2})(TFA)₃ Cartesian coordinates

Atom	x	y	z
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Rh1	-1.61439	0.279621	-1.7795
N2	-2.24326	-0.99637	-0.22839
C3	-2.84752	-2.14556	-0.49285
C4	-3.20554	-3.06033	0.517774
C5	-2.90418	-2.76504	1.824834
C6	-6.38771	1.39229	-1.70982
C7	-5.83733	0.727384	-2.77763
C8	-4.43876	0.544272	-2.8364
N9	-3.62009	1.023647	-1.90787
H10	-3.0245	-2.35516	-1.54203
H11	-3.69854	-3.98544	0.240734
H12	-3.15561	-3.45291	2.62766
O13	-2.19235	-1.14533	-3.07224
H14	-3.97441	-0.01548	-3.63588
O15	0.101071	-0.80221	-1.56803
C16	1.280911	-0.54795	-2.05761
O17	1.805978	0.501458	-2.36579
C18	2.101503	-1.87008	-2.1153
F19	3.231756	-1.71628	-2.81296
F20	2.443295	-2.24407	-0.85442
F21	1.405957	-2.88501	-2.65969
O22	-0.86152	1.58485	-3.13661
C23	-1.40258	1.836345	-4.28347
O24	-2.39649	1.357663	-4.80761
C25	-0.62398	2.976155	-4.99909
F26	-1.09787	3.189633	-6.23314
F27	-0.77347	4.131681	-4.29714
F28	0.687493	2.719676	-5.08767
C29	-1.48887	-1.54203	-4.10643
O30	-0.40844	-1.19311	-4.5149
C31	-2.31647	-2.63248	-4.84733
F32	-1.6402	-3.15524	-5.86883
F33	-2.65208	-3.63959	-4.004
F34	-3.46965	-2.11013	-5.32411
C35	-4.13024	1.77624	-0.87584
C36	-5.53863	1.94508	-0.71807
C37	-6.0278	2.67156	0.397214
C38	-5.15328	3.236845	1.295931
C39	-3.75948	3.128249	1.092117
C40	-3.23967	2.416079	0.026886

H41	-7.10177	2.783372	0.518732
H42	-5.52735	3.795561	2.14826
H43	-3.07875	3.633696	1.77087
C44	-1.91637	-0.66645	1.064718
C45	-2.23759	-1.5543	2.137399
C46	-1.86112	-1.21435	3.461282
C47	-1.17879	-0.04651	3.705622
C48	-0.8613	0.82447	2.64032
C49	-1.22382	0.546595	1.332912
H50	-2.10759	-1.8974	4.268653
H51	-0.87651	0.213384	4.715419
H52	-0.31762	1.741692	2.848037
H53	-6.45095	0.31394	-3.57031
H54	-7.46369	1.514945	-1.61727
C55	-1.77438	2.460047	-0.27136
C56	-0.83904	1.526443	0.262532
C57	0.546765	1.768548	0.066818
C58	0.973961	2.856933	-0.65427
C59	0.043471	3.764504	-1.18289
C60	-1.30783	3.578602	-0.98753
H61	1.284622	1.086205	0.47006
F62	2.26896	3.084518	-0.84961
F63	0.491369	4.819341	-1.85845
H64	-2.00123	4.296443	-1.41012

Table S119. Rh^{III}(bisq^{F2})(TFA)₃ thermodynamic values

Temp	298.15	498.15
E _{gas}	-2919.70	-2919.70
E _{solv}	-2919.74	-2919.74
G	-2919.39	-2919.47
ZPE	254.723	254.723
H _{vib}	24.718	62.731
S _{trans}	45.953	48.504
S _{rot}	38.416	39.947
S _{vib}	166.960	263.990
solv	-24.9	-24.9

Table S120. [Rh^{III}(bisq^{F2})(TFA)₂(TFAH_{eq})]⁺
Cartesian coordinates

Atom	x	y	z
Rh1	-1.1287	0.554888	-1.4208
N2	-1.83655	-0.91296	-0.1364
C3	-2.17941	-2.12284	-0.56325
C4	-2.81857	-3.05476	0.277849
C5	-3.1336	-2.69462	1.567907
C6	-5.61377	2.425531	-1.58131
C7	-5.27043	1.289433	-2.27178
C8	-3.9555	0.804569	-2.17456
N9	-3.02257	1.394285	-1.43051
H10	-1.97397	-2.34294	-1.60396
H11	-3.07058	-4.03179	-0.11836
H12	-3.65638	-3.3824	2.225761
H13	-3.63887	-0.06595	-2.73484
O14	0.63482	-0.62252	-1.31253
C15	1.80331	-0.68918	-1.74463
O16	2.48027	0.161939	-2.39332
C17	2.542599	-2.00438	-1.39419
F18	3.787926	-2.0163	-1.85232
F19	2.563691	-2.13912	-0.0545
F20	1.865913	-3.03875	-1.91472
O21	-0.78188	2.082817	-2.78263
C22	0.283278	2.589913	-3.25279
O23	1.46898	2.274006	-3.07689
C24	-0.00832	3.851661	-4.11063
F25	-0.47116	4.827005	-3.28863
F26	1.084144	4.298006	-4.72094
F27	-0.95229	3.598262	-5.02575
H28	1.951695	1.05089	-2.67346
C29	-3.32191	2.541576	-0.72277
C30	-4.64312	3.087899	-0.79288
C31	-4.94548	4.287992	-0.1004
C32	-3.97498	4.937535	0.622511
C33	-2.67267	4.401416	0.683717
C34	-2.33279	3.219115	0.043538
H35	-5.95265	4.687743	-0.16761
H36	-4.19909	5.861834	1.144562

H37	-1.91188	4.922429	1.257432
C39	-2.0644	-0.54485	1.167701
C40	-2.76522	-1.41487	2.052757
C41	-3.04248	-0.9678	3.369768
C42	-2.62013	0.274861	3.783804
C43	-1.86828	1.100104	2.916442
C44	-1.57914	0.7058	1.621911
H45	-3.58296	-1.6242	4.045015
H46	-2.83116	0.61635	4.791942
H47	-1.48355	2.047229	3.283538
H49	-5.97917	0.761612	-2.89931
H50	-6.61782	2.83552	-1.63923
C51	-0.93136	2.734376	0.163937
C52	-0.60492	1.49307	0.786095
C53	0.772849	1.182859	1.00552
C54	1.758655	2.057148	0.625568
C55	1.420912	3.284481	0.01988
C56	0.103401	3.614558	-0.21659
H59	1.051348	0.258375	1.499378
F56	3.044076	1.77211	0.819992
F57	2.398555	4.104066	-0.33273
H62	-0.1208	4.544241	-0.72661
O59	-1.68568	-0.62919	-2.95176
C60	-0.92016	-0.8243	-4.00311
O61	0.176405	-0.37821	-4.25014
C62	-1.6448	-1.81803	-4.95588
F63	-2.87129	-1.35734	-5.27292
F64	-0.95283	-2.01011	-6.07092
F65	-1.79884	-3.00484	-4.32594

Table S121. $[\text{Rh}^{\text{III}}(\text{bisq}^{\text{F2}})(\text{TFA})_2(\text{TFAH}_{\text{eq}})]^+$
thermodynamic values

Temp	298.15	498.15
E _{gas}	-2920.09	-2920.09
E _{solv}	-2920.16	-2920.16
G	-2919.80	-2919.88
ZPE	262.339	262.339
H _{vib}	25.169	63.621
S _{trans}	45.957	48.507

S _{rot}	38.450	39.981
S _{vib}	166.233	263.342
solv	-44.1	-44.1

Table S122. $[\text{Rh}^{\text{III}}(\text{bisq}^{\text{F2}})(\kappa^1\text{-TFA}_{\text{ax}})(\kappa^2\text{-TFA}_{\text{eq,eq}})]^+$
Cartesian coordinates

Atom	x	y	z
Rh1	-1.30374	0.511259	-1.99079
N2	-2.20688	-0.79105	-0.627
C3	-2.9363	-1.8209	-1.04651
C4	-3.63938	-2.6574	-0.15929
C5	-3.59699	-2.39501	1.189625
C6	-5.51557	2.970912	-1.72994
C7	-5.34866	1.943143	-2.62715
C8	-4.11104	1.276308	-2.68627
N9	-3.08144	1.610522	-1.91297
H10	-2.97048	-1.98024	-2.11728
H11	-4.21024	-3.48601	-0.56265
H12	-4.14495	-3.01104	1.896906
H13	-3.94555	0.457017	-3.37521
O14	-0.1027	1.495635	-3.41618
C15	0.752678	0.560447	-3.31212
O16	0.574176	-0.34009	-2.43234
C17	2.056456	0.608571	-4.12037
F18	2.943045	1.324329	-3.38577
F19	2.546419	-0.61135	-4.31228
F20	1.874885	1.22024	-5.2859
C21	-4.43458	3.363246	-0.90353
C22	-3.19677	2.659704	-1.02688
C23	-2.0731	3.071393	-0.26666
C24	-2.20835	4.142486	0.601056
C25	-3.43712	4.820219	0.755639
C26	-4.53036	4.44121	0.012803
H27	-1.34395	4.473583	1.169387
H28	-3.50514	5.650831	1.450552
H29	-5.47526	4.968598	0.10301
C30	-2.81636	-1.31536	1.670538
C31	-2.09747	-0.52707	0.72049
C32	-1.23696	0.50739	1.163582

C33	-1.14044	0.759337	2.521833
C34	-1.88367	0.016942	3.466213
C35	-2.7003	-1.00913	3.050724
H36	-0.46467	1.53532	2.869592
H37	-1.78611	0.248133	4.521952
H38	-3.25244	-1.60752	3.769052
H39	-6.14662	1.626574	-3.28907
H40	-6.46222	3.497957	-1.65188
C41	-0.72276	2.449549	-0.4454
C42	-0.33669	1.240561	0.213077
C43	1.039031	0.886659	0.24692
C44	1.981707	1.68497	-0.3545
C45	1.598826	2.878828	-1.0022
C46	0.277763	3.257187	-1.04438
H47	1.361388	-0.01565	0.754139
F48	3.268791	1.362835	-0.32971
F49	2.541982	3.62792	-1.558
H50	0.012102	4.18333	-1.54134
O51	-2.13707	-0.59095	-3.46594
C52	-1.60134	-1.00291	-4.59395
O53	-0.49543	-0.83639	-5.05336
C54	-2.67786	-1.83115	-5.35732
F55	-3.06307	-2.88597	-4.60349
F56	-3.7717	-1.07022	-5.58388
F57	-2.2166	-2.27755	-6.51631

Table S123. $[\text{Rh}^{\text{III}}(\text{bisq}^{\text{F2}})(\kappa^1\text{-TFA}_{\text{ax}})(\kappa^2\text{-TFA}_{\text{eq,eq}})]^+$ thermodynamic values

Temp	298.15	498.15
E_{gas}	-2393.30	-2393.30
E_{solv}	-2393.37	-2393.37
G	-2393.04	-2393.11
ZPE	237.700	237.700
H_{vib}	20.316	52.944
S_{trans}	45.506	48.056
S_{rot}	37.757	39.287
S_{vib}	131.415	213.753
solv	-44.9	-44.9

Table S124. $[\text{Rh}^{\text{III}}(\text{bisq}^{\text{F2}})(\kappa^1\text{-TFA}_{\text{eq}})(\kappa^2\text{-TFA}_{\text{ax,eq}})]^+$ Cartesian coordinates

Atom	x	y	z
Rh1	-1.24945	0.487101	-1.88312
N2	-2.23325	-0.72106	-0.48791
C3	-3.05268	-1.70854	-0.83173
C4	-3.72869	-2.49294	0.122157
C5	-3.54112	-2.23023	1.460409
C6	-5.51274	2.738969	-1.9698
C7	-5.16253	1.790242	-2.90208
C8	-3.86928	1.23889	-2.86489
N9	-2.96556	1.613485	-1.96471
H10	-3.16978	-1.89015	-1.89472
H11	-4.3819	-3.28957	-0.21546
H12	-4.0488	-2.81865	2.219461
H13	-3.5555	0.487458	-3.57885
O14	0.245744	-1.05082	-2.22594
C15	-0.47312	-1.47112	-3.16786
O16	-1.59869	-0.90295	-3.4008
C17	-0.0721	-2.69116	-4.0136
F18	-0.79519	-3.7458	-3.5908
F19	-0.3431	-2.46832	-5.30065
F20	1.222073	-2.9597	-3.86378
O21	-0.13147	1.600287	-3.15268
C22	-0.62914	2.093167	-4.25535
O23	-1.75294	1.975903	-4.70355
C24	0.445848	2.939677	-4.99165
F25	-0.05417	3.499547	-6.0913
F26	0.886183	3.926564	-4.17435
F27	1.500511	2.180248	-5.33109
C29	-4.55833	3.182869	-1.02167
C30	-3.25141	2.607469	-1.05734
C31	-2.23471	3.104573	-0.19945
C32	-2.54707	4.116582	0.69158
C33	-3.85275	4.648705	0.775668
C34	-4.83755	4.198702	-0.07174
H35	-1.76752	4.518533	1.331345
H36	-4.06427	5.432564	1.495562
H37	-5.83471	4.627065	-0.04204

C38	-2.67182	-1.18472	1.859515
C39	-2.01782	-0.43272	0.838423
C40	-1.12375	0.612864	1.175103
C41	-0.90012	0.887534	2.512801
C42	-1.54866	0.1565	3.534485
C43	-2.41743	-0.86222	3.216959
H44	-0.20416	1.676214	2.784618
H45	-1.34723	0.401224	4.572438
H46	-2.91167	-1.43504	3.995914
H47	-5.85701	1.451189	-3.66204
H48	-6.50975	3.170309	-1.96039
C49	-0.82255	2.646632	-0.36166
C50	-0.36492	1.374157	0.119003
C51	1.026114	1.058936	-0.01723
C52	1.88205	1.932438	-0.63404
C53	1.412225	3.182661	-1.09428
C54	0.086325	3.539635	-0.95222
H55	1.412054	0.120596	0.36503
F55	3.168119	1.643683	-0.79623
F56	2.274211	4.004725	-1.66324
H58	-0.24305	4.495915	-1.34185

Table S125. $[\text{Rh}^{\text{III}}(\text{bisq}^{\text{F2}})(\kappa^1\text{-TFA}_{\text{eq}})(\kappa^2\text{-TFA}_{\text{ax,eq}})]^+$ thermodynamic values

Temp	298.15	498.15
E_{gas}	-2393.30	-2393.30
E_{solv}	-2393.38	-2393.38
G	-2393.05	-2393.11
ZPE	237.412	237.412
H_{vib}	20.526	53.186
S_{trans}	45.506	48.056
S_{rot}	37.698	39.228
S_{vib}	133.138	215.558
solv	-46.0	-46.0

Table S126. $[\text{Rh}^{\text{III}}(\text{bisq}^{\text{F2}})(\text{Me}_{\text{ax}})(\text{TFA}_{\text{eq}})(\text{TFAH}_{\text{eq}})]^+$ Cartesian coordinates

Atom	x	y	z
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Rh1	-1.19453	0.485964	-1.54096
N2	-1.76063	-0.98985	-0.17516
C3	-1.94653	-2.25807	-0.52538
C4	-2.5947	-3.19064	0.305798
C5	-3.0962	-2.76765	1.515075
C6	-5.59705	2.575878	-1.36776
C7	-5.41708	1.312575	-1.87445
C8	-4.13117	0.752094	-1.83929
N9	-3.07008	1.36714	-1.3202
H10	-1.58797	-2.54874	-1.50475
H11	-2.71459	-4.21187	-0.03762
H12	-3.65081	-3.44568	2.157029
H13	-3.96309	-0.22453	-2.26943
O14	0.594759	-0.66066	-1.5988
C15	1.818854	-0.56437	-1.80482
O16	2.466916	0.362275	-2.38321
C17	2.681059	-1.71468	-1.23098
F18	3.912772	-1.71305	-1.72684
F19	2.743754	-1.55642	0.106638
F20	2.099067	-2.89353	-1.49148
O21	-0.91492	2.070062	-2.87047
C22	0.099844	2.569454	-3.4384
O23	1.289358	2.205334	-3.43659
C24	-0.23229	3.878666	-4.20256
F25	-0.50507	4.844228	-3.29119
F26	0.78245	4.285664	-4.95895
F27	-1.31694	3.717697	-4.97401
H28	1.86079	1.154986	-2.81087
C29	-3.22747	2.607936	-0.72676
C30	-4.5062	3.255543	-0.7782
C31	-4.66683	4.556672	-0.23717
C32	-3.60628	5.196603	0.353489
C33	-2.36278	4.540143	0.447541
C34	-2.15051	3.267053	-0.06145
H35	-5.64207	5.029775	-0.30026
H36	-3.71946	6.193883	0.765899
H37	-1.54189	5.037219	0.955704
C38	-2.11252	-0.57497	1.092787
C39	-2.86287	-1.43863	1.947598
C40	-3.30894	-0.95024	3.203121

C41	-2.98296	0.323473	3.605552
C42	-2.14618	1.129643	2.800684
C43	-1.69412	0.701473	1.564899
H44	-3.89266	-1.60411	3.844574
H45	-3.32067	0.697982	4.566508
H46	-1.81191	2.091227	3.178752
H47	-6.22836	0.749261	-2.32097
H48	-6.56686	3.063618	-1.40461
C49	-0.80329	2.664468	0.142069
C50	-0.60492	1.461655	0.862377
C51	0.717035	1.034252	1.130832
C52	1.799271	1.777132	0.706762
C53	1.599629	2.973967	0.006199
C54	0.320644	3.409853	-0.27749
H55	0.901887	0.124074	1.69069
F56	3.044688	1.36441	0.948591
F57	2.660973	3.667549	-0.39947
H58	0.194409	4.320247	-0.85258
C59	-1.73637	-0.54412	-3.23678
H60	-2.19063	0.181613	-3.91127
H61	-0.81173	-0.94204	-3.65744
H62	-2.42761	-1.35548	-3.0019

Table S127. $[\text{Rh}^{\text{III}}(\text{bisq}^{\text{F2}})(\text{Me}_{\text{ax}})(\text{TFA}_{\text{eq}})(\text{TFAH}_{\text{eq}})]^+$
thermodynamic values

Temp	298.15	498.15
E_{gas}	-2433.82	-2433.82
E_{solv}	-2433.89	-2433.89
G	-2433.51	-2433.59
ZPE	267.123	267.123
H_{vib}	21.524	56.037
S_{trans}	45.573	48.123
S_{rot}	37.809	39.340
S_{vib}	143.984	232.078
solv	-42.9	-42.9

Table S128. $[\text{Rh}^{\text{III}}(\text{bisq}^{\text{F2}})(\text{Me}_{\text{eq}})(\text{TFA}_{\text{ax}})(\text{TFAH}_{\text{eq}})]^+$
Cartesian coordinates

Atom	x	y	z
Rh1	-1.49131	0.457865	-2.01575
N2	-2.13314	-0.98753	-0.11444
C3	-2.80476	-2.06289	-0.50835
C4	-3.24301	-3.08438	0.358497
C5	-2.95145	-2.9826	1.695253
C6	-6.18701	1.551873	-1.93892
C7	-5.64498	0.993771	-3.07383
C8	-4.26298	0.727344	-3.12053
N9	-3.4516	1.028606	-2.11185
H10	-2.99966	-2.1428	-1.57168
H11	-3.7861	-3.93113	-0.04685
H12	-3.25358	-3.75346	2.398892
O13	-2.07421	-1.10867	-3.21788
H14	-3.81844	0.224475	-3.96886
O15	0.555997	-0.0189	-1.68603
C16	1.555198	-0.51982	-2.22532
O17	1.655721	-1.13059	-3.34122
C18	2.894689	-0.36368	-1.4622
F19	3.829409	-1.18555	-1.92414
F20	3.313483	0.906784	-1.59908
F21	2.69836	-0.6077	-0.15617
H22	0.747967	-1.29768	-3.84956
C23	-1.53768	-1.756	-4.1777
O24	-0.37203	-1.75521	-4.5879
C25	-2.58311	-2.63864	-4.9112
F26	-2.03151	-3.3826	-5.86012
F27	-3.2058	-3.44138	-4.02701
F28	-3.51479	-1.83454	-5.47144
C29	-3.94924	1.640843	-0.98292
C30	-5.34659	1.8855	-0.84796
C31	-5.82881	2.436105	0.36746
C32	-4.95407	2.733763	1.387181
C33	-3.56502	2.530884	1.222007
C34	-3.04984	2.001805	0.05182
H35	-6.89431	2.613976	0.478161
H36	-5.32253	3.149693	2.319431
H37	-2.88751	2.816617	2.02063
C38	-1.85232	-0.84615	1.226288
C39	-2.23861	-1.85391	2.16889

C40	-1.90195	-1.71878	3.540083
C41	-1.19837	-0.62343	3.979019
C42	-0.82208	0.378512	3.061456
C43	-1.13963	0.29786	1.713314
H44	-2.20767	-2.49903	4.231341
H45	-0.93528	-0.51936	5.026709
H46	-0.28197	1.24925	3.422007
H47	-6.2589	0.730305	-3.92754
H48	-7.25426	1.739029	-1.86509
C49	-1.57035	1.941846	-0.17768
C50	-0.68182	1.356041	0.788346
C51	0.64649	1.753153	0.812646
C52	1.140647	2.683807	-0.10909
C53	0.322643	3.190863	-1.10248
C54	-1.02836	2.835762	-1.13933
H55	1.349706	1.302592	1.504352
F56	2.417231	3.047764	-0.0572
F57	0.811927	4.032447	-2.01692
H58	-1.68135	3.387643	-1.80514
C59	-1.00892	1.513011	-3.73958
H60	-0.90214	0.78273	-4.54148
H61	-1.80725	2.219464	-3.97447
H62	-0.06768	2.041584	-3.58634

Table S129. $[\text{Rh}^{\text{III}}(\text{bisq}^{\text{F2}})(\text{Me}_{\text{eq}})(\text{TFA}_{\text{ax}})(\text{TFAH}_{\text{eq}})]^+$ thermodynamic values

Temp	298.15	498.15
E_{gas}	-2433.81	-2433.81
E_{solv}	-2433.87	-2433.87
G	-2433.50	-2433.57
ZPE	267.678	267.678
H_{vib}	22.092	57.002
S_{trans}	45.573	48.123
S_{rot}	37.930	39.460
S_{vib}	143.570	231.673
solv	-40.6	-40.644

Table S130. $\text{Rh}^{\text{III}}(\text{bisq}^{\text{F2}})(\text{Me}_{\text{ax}})(\text{TFA})_2$ Cartesian coordinates

Atom	x	y	z
Rh1	-1.7515	0.229269	-1.81143
N2	-2.42783	-0.89022	-0.13668
C3	-3.27639	-1.89804	-0.29938
C4	-3.6031	-2.81374	0.717731
C5	-2.98943	-2.68631	1.938603
C6	-6.4568	1.50842	-1.7467
C7	-5.89698	1.078782	-2.92515
C8	-4.50289	0.863755	-2.98968
N9	-3.69492	1.099878	-1.96188
H10	-3.70065	-2.01189	-1.2886
H11	-4.30246	-3.6152	0.506897
H12	-3.17713	-3.39501	2.740544
H13	-4.01862	0.505508	-3.89178
O14	0.062564	-0.62814	-1.41515
C15	0.94194	-0.98934	-2.2988
O16	0.881933	-1.04763	-3.51147
C17	2.24776	-1.42407	-1.57252
F18	3.211321	-1.76224	-2.43548
F19	2.732079	-0.4263	-0.78874
F20	2.021074	-2.48715	-0.76655
O21	-0.89074	1.414337	-3.22256
C22	-1.30641	1.612419	-4.42437
O23	-2.28904	1.167164	-5.00657
C24	-0.37135	2.611414	-5.16002
F25	-0.74897	2.794335	-6.43327
F26	-0.41053	3.818753	-4.54292
F27	0.905047	2.192494	-5.15811
C28	-4.20755	1.684261	-0.82182
C29	-5.61678	1.833561	-0.65076
C30	-6.1188	2.3264	0.581589
C31	-5.25127	2.70078	1.580731
C32	-3.85512	2.656632	1.362451
C33	-3.31983	2.174374	0.181991
H34	-7.19358	2.417444	0.71156
H35	-5.63229	3.080204	2.524015
H36	-3.18384	3.048612	2.120951

C37	-1.86497	-0.67578	1.105185
C38	-2.09899	-1.60973	2.166205
C39	-1.44789	-1.4454	3.41483
C40	-0.6088	-0.37856	3.618656
C41	-0.42872	0.575149	2.595913
C42	-1.04214	0.465982	1.357134
H43	-1.62709	-2.17711	4.197389
H44	-0.09879	-0.24862	4.568145
H45	0.197901	1.44144	2.785173
H46	-6.50209	0.866849	-3.79994
H47	-7.53224	1.628859	-1.64519
C48	-1.86637	2.365298	-0.13531
C49	-0.81598	1.571332	0.38124
C50	0.519013	1.924691	0.086177
C51	0.795315	3.026962	-0.69441
C52	-0.24173	3.818671	-1.19573
C53	-1.55265	3.496839	-0.91642
H54	1.338594	1.296041	0.410852
F55	2.058153	3.351088	-0.99238
F56	0.052981	4.88888	-1.93899
H57	-2.33875	4.126287	-1.3187
C58	-2.13967	-1.31429	-3.10492
H59	-1.61076	-1.0958	-4.02749
H60	-1.74483	-2.21961	-2.63944
H61	-3.21695	-1.39728	-3.27562

Table S131. Rh^{III}(bisq^{F2})(Me_{ax})(TFA)₂
thermodynamic values

Temp	298.15	498.15
E_{gas}	-2433.43	-2433.43
E_{solv}	-2433.47	-2433.47
G	-2433.10	-2433.17
ZPE	260.233	260.233
H_{vib}	22.000	56.776
S_{trans}	45.569	48.119
S_{rot}	37.797	39.327
S_{vib}	143.067	230.845
solv	-23.0	-23.0

Table S132. Rh^{III}(bisq^{F2})(Me_{eq})(TFA)₂ Cartesian
coordinates

Atom	x	y	z
Rh1	-1.47266	0.560031	-2.13036
N2	-2.27386	-0.85517	-0.17024
C3	-3.0255	-1.86579	-0.57253
C4	-3.48376	-2.89672	0.276795
C5	-3.12914	-2.86234	1.601134
C6	-6.18843	1.722831	-1.94548
C7	-5.67667	1.156831	-3.08933
C8	-4.2952	0.878424	-3.16345
N9	-3.46181	1.175038	-2.1759
H10	-3.28985	-1.87784	-1.6238
H11	-4.08773	-3.69867	-0.1341
H12	-3.44237	-3.64284	2.289935
O13	-2.03678	-0.8999	-3.42636
H14	-3.85496	0.365729	-4.01197
O15	0.452947	0.01241	-1.80355
C16	1.285566	-0.4719	-2.67213
O17	1.170254	-0.6409	-3.87104
C18	2.617662	-0.83231	-1.95541
F19	3.521785	-1.33436	-2.80437
F20	3.161793	0.27347	-1.38227
F21	2.423078	-1.73381	-0.97127
C22	-1.58498	-2.12222	-3.42729
O23	-0.80498	-2.6814	-2.68548
C24	-2.33864	-2.9314	-4.51898
F25	-1.78812	-4.13062	-4.72295
F26	-3.62145	-3.13066	-4.10045
F27	-2.39975	-2.28736	-5.69839
C28	-3.93037	1.784793	-1.03626
C29	-5.32173	2.046024	-0.86992
C30	-5.77719	2.590133	0.358163
C31	-4.88153	2.861761	1.366235
C32	-3.49894	2.636327	1.177578
C33	-3.00591	2.116025	-0.00574
H34	-6.83906	2.778952	0.488959
H35	-5.22898	3.269256	2.310789
H36	-2.80473	2.890876	1.972392

C37	-1.93421	-0.77808	1.1553
C38	-2.34006	-1.78894	2.084891
C39	-1.95394	-1.7024	3.446382
C40	-1.18977	-0.64807	3.884962
C41	-0.79496	0.358121	2.978742
C42	-1.15182	0.321034	1.639799
H43	-2.27235	-2.48405	4.130647
H44	-0.89122	-0.57991	4.926725
H45	-0.20241	1.194254	3.339124
H46	-6.31353	0.895544	-3.92736
H47	-7.25241	1.920953	-1.84704
C48	-1.52844	2.007037	-0.23161
C49	-0.66091	1.364056	0.712236
C50	0.6963	1.652063	0.693947
C51	1.233851	2.547087	-0.23396
C52	0.422528	3.134399	-1.18271
C53	-0.95049	2.86552	-1.19934
H54	1.381962	1.130726	1.352401
F55	2.540836	2.813889	-0.22053
F56	0.942351	3.967859	-2.09369
H57	-1.57669	3.461452	-1.85247
C58	-0.99464	1.598017	-3.85124
H59	-0.91485	0.834741	-4.62148
H60	-1.79204	2.315734	-4.06786
H61	-0.03989	2.105621	-3.7175

Table S133. $\text{Rh}^{\text{III}}(\text{bisq}^{\text{F2}})(\text{Me}_{\text{eq}})(\text{TFA})_2$
thermodynamic values

Temp	298.15	498.15
E_{gas}	-2433.42	-2433.42
E_{solv}	-2433.45	-2433.45
G	-2433.09	-2433.16
ZPE	259.808	259.808
H_{vib}	22.238	57.066
S_{trans}	45.569	48.119
S_{rot}	37.843	39.373
S_{vib}	144.511	232.422
solv	-21.1	-21.1

Table S134. $[\text{Rh}^{\text{IV}}(\text{bisq}^{\text{F2}})(\text{Me}_{\text{ax}})(\text{TFA})_2]^+$ Cartesian coordinates

Atom	x	y	z
Rh1	-1.75613	0.201817	-1.7943
N2	-2.44291	-0.89273	-0.12788
C3	-3.29971	-1.90034	-0.29922
C4	-3.6399	-2.80563	0.714738
C5	-3.03442	-2.67204	1.943549
C6	-6.45822	1.467622	-1.70923
C7	-5.91366	0.984781	-2.87774
C8	-4.52787	0.755764	-2.94054
N9	-3.70578	1.029496	-1.92621
H10	-3.72074	-2.01431	-1.2895
H11	-4.34055	-3.60512	0.503111
H12	-3.23459	-3.37765	2.744813
H13	-4.06775	0.352607	-3.83354
O14	0.016181	-0.6557	-1.4532
C15	0.938499	-0.80264	-2.37177
O16	0.8746	-0.54647	-3.55858
C17	2.2476	-1.35303	-1.73916
F18	3.175805	-1.56614	-2.66453
F19	2.725322	-0.46767	-0.83935
F20	1.991135	-2.50573	-1.09769
O21	-0.96285	1.397051	-3.13915
C22	-1.29712	1.565399	-4.40499
O23	-2.26452	1.101736	-4.97324
C24	-0.31371	2.536568	-5.10866
F25	-0.62599	2.666006	-6.39579
F26	-0.40132	3.745971	-4.51498
F27	0.946387	2.101298	-4.99996
C28	-4.20055	1.662385	-0.79934
C29	-5.60971	1.827647	-0.63301
C30	-6.10675	2.381799	0.574542
C31	-5.23663	2.797743	1.555509
C32	-3.84291	2.730793	1.337449
C33	-3.31037	2.186299	0.180464
H34	-7.18023	2.489186	0.699179
H35	-5.61376	3.226904	2.478155
H36	-3.16822	3.154763	2.075347

C37	-1.88624	-0.66901	1.118752
C38	-2.14116	-1.60181	2.177322
C39	-1.49988	-1.44281	3.432251
C40	-0.64732	-0.38648	3.642196
C41	-0.44466	0.561182	2.619646
C42	-1.05222	0.460765	1.37407
H43	-1.69437	-2.1701	4.214551
H44	-0.14508	-0.26105	4.595793
H45	0.190607	1.419582	2.815794
H46	-6.52691	0.746513	-3.73934
H47	-7.53153	1.602371	-1.60681
C48	-1.85404	2.361695	-0.13308
C49	-0.81051	1.566144	0.402746
C50	0.528949	1.924084	0.131586
C51	0.820128	3.026923	-0.64443
C52	-0.21111	3.818984	-1.16563
C53	-1.52716	3.495722	-0.90664
H54	1.347488	1.311423	0.490399
F55	2.082268	3.348773	-0.91962
F56	0.095321	4.879563	-1.90708
H57	-2.30617	4.134282	-1.30888
C58	-2.10035	-1.35087	-3.12781
H59	-1.5549	-1.11161	-4.03507
H60	-1.69814	-2.23694	-2.6372
H61	-3.17117	-1.43534	-3.30569

Table S135. $[\text{Rh}^{\text{IV}}(\text{bisq}^{\text{F2}})(\text{Me}_{\text{ax}})(\text{TFA})_2]^+$ thermodynamic values

Temp	298.15	498.15
E_{gas}	-2433.14	-2433.14
E_{solv}	-2433.22	-2433.22
G	-2432.86	-2432.93
ZPE	260.214	260.214
H_{vib}	21.956	56.750
S_{trans}	45.569	48.119
S_{rot}	37.768	39.298
S_{vib}	142.454	230.274
solv	-48.7	-48.7

Table S136. $[\text{Rh}^{\text{IV}}(\text{bisq}^{\text{F2}})(\text{Me}_{\text{eq}})(\text{TFA})_2]^+$ Cartesian coordinates

Atom	x	y	z
Rh1	-1.48696	0.586243	-2.12666
N2	-2.35745	-0.84095	-0.21407
C3	-3.18426	-1.80598	-0.59159
C4	-3.64592	-2.82574	0.264027
C5	-3.21426	-2.83459	1.5686
C6	-6.20728	1.79835	-2.00662
C7	-5.68906	1.264042	-3.16489
C8	-4.31022	0.976235	-3.23518
N9	-3.48571	1.238457	-2.22934
H10	-3.4946	-1.79175	-1.63106
H11	-4.30937	-3.5909	-0.1235
H12	-3.52021	-3.61606	2.258445
O13	-2.06639	-0.92568	-3.28379
H14	-3.87081	0.493881	-4.10183
O15	0.41034	0.018241	-1.73954
C16	1.255172	-0.48506	-2.60176
O17	1.117001	-0.67681	-3.79089
C18	2.58685	-0.81719	-1.8733
F19	3.509613	-1.26765	-2.71667
F20	3.067737	0.305554	-1.27439
F21	2.39057	-1.7338	-0.90937
C22	-1.55036	-2.14546	-3.27463
O23	-0.78578	-2.64695	-2.48787
C24	-2.20753	-2.96704	-4.41742
F25	-1.63533	-4.15881	-4.54572
F26	-3.51694	-3.14867	-4.10488
F27	-2.14855	-2.32045	-5.59051
C28	-3.96266	1.806765	-1.07337
C29	-5.34981	2.077055	-0.91098
C30	-5.8044	2.582585	0.335553
C31	-4.91295	2.80273	1.360749
C32	-3.53097	2.559896	1.179092
C33	-3.04492	2.076429	-0.02178
H34	-6.8632	2.784481	0.468033
H35	-5.26278	3.183034	2.315076
H36	-2.84321	2.777278	1.990724

C37	-1.95731	-0.79546	1.089894
C38	-2.3504	-1.80695	2.02003
C39	-1.85569	-1.78056	3.349314
C40	-0.98949	-0.78713	3.759199
C41	-0.6005	0.213144	2.856117
C42	-1.08408	0.251724	1.544962
H43	-2.15941	-2.56622	4.035521
H44	-0.61115	-0.77141	4.775888
H45	0.059121	1.004071	3.200039
H46	-6.31996	1.037439	-4.017
H47	-7.27034	2.002934	-1.91564
C48	-1.57659	1.949913	-0.29039
C49	-0.66224	1.32411	0.648877
C50	0.690834	1.699877	0.645074
C51	1.182143	2.592228	-0.2913
C52	0.330692	3.133715	-1.26546
C53	-1.03272	2.831384	-1.26764
H54	1.402838	1.216038	1.303739
F55	2.461706	2.913551	-0.31528
F56	0.829059	3.950097	-2.17713
H57	-1.68354	3.429181	-1.89481
C58	-0.99227	1.529015	-3.91922
H59	-0.90346	0.707276	-4.62375
H60	-1.79812	2.222364	-4.16327
H61	-0.03734	2.034628	-3.7908

Table S137. $[\text{Rh}^{\text{IV}}(\text{bisq}^{\text{F2}})(\text{Me}_{\text{eq}})(\text{TFA})_2]^+$
thermodynamic values

Temp	298.15	498.15
E_{gas}	-2433.13	-2433.13
E_{solv}	-2433.22	-2433.22
G	-2432.85	-2432.93
ZPE	259.636	259.636
H_{vib}	21.678	56.152
S_{trans}	45.569	48.119
S_{rot}	37.794	39.324
S_{vib}	144.537	232.563
solv	-50.6	-50.6

Table S138. $[\text{Rh}^{\text{III}}(\text{bisq}^{\text{F2}})(\text{Me}_{\text{ax}}\cdots\text{H}_{\text{eq}})(\text{TFA}_{\text{eq}})]^{\ddagger}$
Cartesian coordinates

Atom	x	y	z
Rh1	-1.54317	0.329782	-2.05039
N2	-2.33414	-1.02488	0.206671
C3	-3.07402	-2.08072	-0.06721
C4	-3.51319	-3.01196	0.901626
C5	-3.14112	-2.81657	2.208778
C6	-6.20919	1.751763	-1.89854
C7	-5.72372	1.183629	-3.05232
C8	-4.36217	0.830278	-3.12625
N9	-3.50088	1.038006	-2.13545
H10	-3.34098	-2.22058	-1.11347
H11	-4.12083	-3.8598	0.602008
H12	-3.44449	-3.50985	2.989391
H13	-3.96719	0.346453	-4.01049
O14	0.326115	-0.4278	-1.72132
C15	1.291694	-0.36831	-2.57614
O16	1.32037	0.0956	-3.70613
C17	2.577541	-0.99899	-1.97328
F18	3.601931	-0.97125	-2.83643
F19	2.963805	-0.33112	-0.85853
F20	2.372776	-2.28729	-1.6192
H21	-1.30392	0.371211	-3.60448
C28	-3.94544	1.67565	-0.99347
C29	-5.32208	2.011805	-0.82462
C30	-5.74748	2.582797	0.402104
C31	-4.83524	2.824271	1.402465
C32	-3.46503	2.543099	1.205288
C33	-3.00033	1.984597	0.026632
H34	-6.79879	2.823465	0.533141
H35	-5.1588	3.258787	2.343721
H36	-2.7534	2.78949	1.986671
C37	-1.95997	-0.80074	1.501492
C38	-2.34147	-1.69685	2.551803
C39	-1.91446	-1.45655	3.882412
C40	-1.12407	-0.36835	4.165132
C41	-0.74296	0.519078	3.135347
C42	-1.14291	0.336793	1.820274

H43	-2.21898	-2.146	4.6656
H44	-0.79093	-0.18133	5.181781
H45	-0.12367	1.377837	3.377997
H46	-6.3672	0.982461	-3.90203
H47	-7.25985	2.00936	-1.79661
C48	-1.53842	1.814751	-0.22441
C49	-0.659	1.254102	0.761028
C50	0.704007	1.50473	0.677972
C51	1.229523	2.301938	-0.34363
C52	0.409213	2.813404	-1.326
C53	-0.97091	2.557772	-1.30176
H54	1.39896	1.036079	1.365201
F49	2.546389	2.545893	-0.38253
F50	0.920648	3.575839	-2.30138
H57	-1.59815	3.144561	-1.96241
C58	-1.71712	-1.0714	-3.69858
H59	-2.43529	-0.90465	-4.50577
H60	-0.76259	-1.37964	-4.12172
H61	-2.09889	-1.86909	-3.04962

Table S139. $[\text{Rh}^{\text{I-III}}(\text{bisq}^{\text{F2}})(\text{Me}_{\text{ax}}\cdots\text{H}_{\text{eq}})(\text{TFA}_{\text{eq}})]^{\ddagger}$
thermodynamic values

Temp	298.15	498.15
E_{gas}	-1907.82	-1907.82
E_{solv}	-1907.85	-1907.85
G	-1907.50	-1907.57
ZPE	244.764	244.764
H_{vib}	18.121	47.667
S_{trans}	45.059	47.609
S_{rot}	37.021	38.551
S_{vib}	117.456	191.955
solv	-17.5	-17.5

Table S140. $[\text{Rh}^{\text{I-III}}(\text{bisq}^{\text{F2}})(\text{Me}_{\text{eq}}\cdots\text{H}_{\text{ax}})(\text{TFA}_{\text{eq}})]^{\ddagger}$
Cartesian coordinates

Atom	x	y	z
Rh1	-1.42968	0.236939	-1.6871
N2	-1.55548	-1.16426	0.040886

C3	-1.68393	-2.45125	-0.26284
C4	-2.17838	-3.40792	0.652466
C5	-2.56968	-2.99897	1.904015
C6	-6.18124	1.310968	-1.07085
C7	-5.72734	0.203688	-1.74221
C8	-4.33994	-0.00749	-1.83682
N9	-3.4247	0.796217	-1.29559
H10	-1.37817	-2.72525	-1.2698
H11	-2.25779	-4.4445	0.34227
H12	-2.98476	-3.70118	2.622701
H13	-1.78078	0.005042	-3.18729
H14	-3.94848	-0.85788	-2.38258
O15	0.516659	-0.28679	-2.09507
C16	0.797078	-1.44284	-2.57904
O17	0.064163	-2.39497	-2.83694
C18	2.321927	-1.58127	-2.83691
F19	2.634544	-2.77701	-3.36075
F20	2.763411	-0.63215	-3.69003
F21	3.01589	-1.44774	-1.68309
C28	-3.84868	1.901522	-0.58059
C29	-5.24959	2.195661	-0.47616
C30	-5.6869	3.361503	0.20252
C31	-4.77432	4.219137	0.763266
C32	-3.39836	3.920918	0.683971
C33	-2.91477	2.788155	0.047569
H34	-6.75354	3.559941	0.261434
H35	-5.10132	5.118112	1.276984
H36	-2.68312	4.591477	1.151321
C37	-1.85732	-0.74238	1.311802
C38	-2.41579	-1.63922	2.275526
C39	-2.78107	-1.15237	3.556403
C40	-2.57608	0.167992	3.87872
C41	-1.96776	1.038429	2.946246
C42	-1.59928	0.611675	1.682562
H43	-3.21487	-1.84204	4.275804
H44	-2.85317	0.543805	4.859231
H45	-1.75894	2.064662	3.234417
H46	-6.40485	-0.501	-2.21202
H47	-7.2429	1.527422	-0.98839
C48	-1.4361	2.577924	0.056483

C49	-0.8272	1.537667	0.792457
C50	0.57476	1.446821	0.817668
C51	1.354286	2.370753	0.145048
C52	0.752364	3.422645	-0.5428
C53	-0.62615	3.533791	-0.58056
H54	1.069046	0.652745	1.366527
F49	2.690315	2.282841	0.17012
F50	1.523704	4.326411	-1.16578
H57	-1.06783	4.35274	-1.13779
C58	-1.36307	1.432536	-3.49126
H59	-0.81859	1.057322	-4.36165
H60	-2.31877	1.858251	-3.80662
H61	-0.74433	2.205334	-3.02495

Table S141. $[\text{Rh}^{\text{I-III}}(\text{bisq}^{\text{F2}})(\text{Me}_{\text{eq}}\cdots\text{H}_{\text{ax}})(\text{TFA}_{\text{eq}})]^{\ddagger}$
thermodynamic values

Temp	298.15	498.15
E_{gas}	-1907.83	-1907.83
E_{solv}	-1907.86	-1907.86
G	-1907.51	-1907.57
ZPE	245.147	245.147
H_{vib}	17.550	46.623
S_{trans}	45.059	47.609
S_{rot}	37.114	38.644
S_{vib}	117.282	191.586
solv	-16.8	-16.8

Table S142. $[\text{Rh}^{\text{I-III}}(\text{bisq}^{\text{F2}})(\text{Me}_{\text{eq}}\cdots\text{H}_{\text{eq}})(\text{TFA}_{\text{ax}})]^{\ddagger}$
Cartesian coordinates

Atom	x	y	z
Rh1	-1.37428	0.375927	-1.90844
N2	-2.35177	-0.92566	-0.44306
C3	-3.12349	-1.95582	-0.75488
C4	-3.63436	-2.84225	0.218826
C5	-3.31801	-2.64516	1.542279
C6	-6.45765	1.575206	-1.57685
C7	-6.07245	0.889195	-2.70435
C8	-4.68939	0.694121	-2.94646

N9	-3.7508	1.163375	-2.15049
H10	-3.31676	-2.097	-1.81353
H11	-4.26049	-3.67055	-0.09594
H12	-3.68829	-3.31565	2.313414
O13	-1.97921	-0.99234	-3.31308
H14	-4.34032	0.117315	-3.80116
H15	0.119661	0.334346	-2.37939
C22	-1.24608	-1.79443	-4.01443
O23	-0.03795	-1.94154	-4.05242
C24	-2.16726	-2.67938	-4.90166
F25	-1.4742	-3.50526	-5.6922
F26	-2.98335	-3.44111	-4.12569
F27	-2.96562	-1.92184	-5.68923
C28	-4.10401	1.854693	-1.03002
C29	-5.47211	2.078628	-0.68635
C30	-5.78028	2.770648	0.512008
C31	-4.76641	3.216586	1.328883
C32	-3.41239	3.004611	0.977039
C33	-3.06317	2.335032	-0.18262
H34	-6.82181	2.939877	0.773785
H35	-4.99993	3.744848	2.248716
H36	-2.6297	3.383776	1.627788
C37	-2.01944	-0.70345	0.865855
C38	-2.48127	-1.55954	1.907704
C39	-2.06206	-1.30797	3.238778
C40	-1.21191	-0.25983	3.506247
C41	-0.75904	0.583235	2.46485
C42	-1.15538	0.387291	1.152894
H43	-2.40978	-1.96167	4.034105
H44	-0.88231	-0.07097	4.523617
H45	-0.09478	1.409978	2.700456
H46	-6.80326	0.487733	-3.39941
H47	-7.50921	1.733773	-1.34998
C48	-1.6059	2.229362	-0.5727
C49	-0.6893	1.310115	0.064435
C50	0.714108	1.635262	0.060984
C51	1.168777	2.777045	-0.53082
C52	0.267713	3.680312	-1.14806
C53	-1.07204	3.422903	-1.16853
H54	1.420816	0.969587	0.544493

F49	2.476255	3.08092	-0.54723
F50	0.770252	4.795745	-1.69946
H57	-1.74303	4.148569	-1.61486
C58	-0.16014	1.325114	-3.46226
H59	0.159267	0.633645	-4.24136
H60	-0.98504	1.938331	-3.83471
H61	0.665693	1.981706	-3.18304

Table S143. $[\text{Rh}^{\text{III}}(\text{bisq}^{\text{F2}})(\text{Me}_{\text{eq}}\cdots\text{H}_{\text{eq}})(\text{TFA}_{\text{ax}})]^{\ddagger}$
thermodynamic values

Temp	298.15	498.15
E_{gas}	-1907.82	-1907.82
E_{solv}	-1907.84	-1907.84
G	-1907.49	-1907.56
ZPE	244.707	244.707
H_{vib}	18.122	47.689
S_{trans}	45.059	47.609
S_{rot}	37.162	38.692
S_{vib}	116.813	191.368
solv	-15.1	-15.1

Table S144. $[\text{Rh}^{\text{III}}(\text{bisq}^{\text{F2}})(\text{H}_{\text{ax}}\cdots\text{TFA}_{\text{eq}})(\text{Me}_{\text{eq}})]^{\ddagger}$
Cartesian coordinates

Atom	x	y	z
Rh1	-1.39517	0.533538	-1.93364
N2	-2.06558	-0.70801	-0.03372
C3	-2.76746	-1.77613	-0.39099
C4	-3.22501	-2.76233	0.507453
C5	-2.90666	-2.63513	1.836427
C6	-6.10076	1.604971	-1.92691
C7	-5.48858	1.162877	-3.07492
C8	-4.09078	0.985592	-3.08438
N9	-3.30853	1.256192	-2.03783
H10	-2.97464	-1.86637	-1.45269
H11	-3.80009	-3.60351	0.1343
H12	-3.21532	-3.37975	2.565875
H13	-1.21413	-0.96415	-3.07407
H14	-3.58675	0.577788	-3.95166

O15	0.570487	-0.40621	-1.87406
C16	0.572616	-1.37006	-2.64953
O17	-0.44216	-1.75212	-3.35154
C18	1.839625	-2.22076	-2.82839
F19	1.583392	-3.49976	-2.49111
F20	2.24141	-2.19351	-4.11129
F21	2.838115	-1.77309	-2.05884
C28	-3.88414	1.827559	-0.91381
C29	-5.30571	1.948932	-0.80509
C30	-5.88092	2.408541	0.407511
C31	-5.079	2.765093	1.464274
C32	-3.67553	2.727787	1.324149
C33	-3.06377	2.287129	0.162023
H34	-6.963	2.474756	0.480466
H35	-5.51566	3.110424	2.396828
H36	-3.05081	3.081747	2.138236
C37	-1.7738	-0.5315	1.298235
C38	-2.16046	-1.51234	2.271698
C39	-1.79676	-1.35459	3.633251
C40	-1.07451	-0.2563	4.030017
C41	-0.72142	0.728669	3.084402
C42	-1.06109	0.631547	1.742737
H43	-2.09835	-2.11633	4.347431
H44	-0.78661	-0.12949	5.069571
H45	-0.18237	1.610667	3.417845
H46	-6.05926	0.912479	-3.96304
H47	-7.18092	1.70523	-1.86297
C48	-1.57903	2.455889	0.039681
C49	-0.65529	1.740939	0.837616
C50	0.694153	2.130369	0.838474
C51	1.124344	3.196568	0.068246
C52	0.215846	3.902223	-0.71577
C53	-1.12139	3.546363	-0.72215
H54	1.426378	1.585747	1.42388
F49	2.4163	3.564241	0.072851
F50	0.647495	4.940558	-1.45097
H57	-1.81009	4.125745	-1.32722
C58	-0.83378	1.493562	-3.66676
H59	-0.392	0.812264	-4.40745
H60	-1.67159	2.012973	-4.15325

H61	-0.07379	2.244486	-3.40901
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Table S145. $[\text{Rh}^{\text{I-III}}(\text{bisq}^{\text{F2}})(\text{H}_{\text{ax}}\cdots\text{TFA}_{\text{eq}})(\text{Me}_{\text{eq}})]^{\ddagger}$
thermodynamic values

Temp	298.15	498.15
E_{gas}	-1907.82	-1907.82
E_{solv}	-1907.84	-1907.84
G	-1907.49	-1907.55
ZPE	244.323	244.323
H_{vib}	17.931	47.402
S_{trans}	45.059	47.609
S_{rot}	37.180	38.710
S_{vib}	115.966	190.259
solv	-11.3	-11.3

Table S146. $[\text{Rh}^{\text{I-III}}(\text{bisq}^{\text{F2}})(\text{H}_{\text{eq}}\cdots\text{TFA}_{\text{ax}})(\text{Me}_{\text{eq}})]^{\ddagger}$
Cartesian coordinates

Atom	x	y	z
Rh1	-1.6584	0.460629	-2.00974
N2	-2.609	-0.83816	-0.48023
C3	-3.50838	-1.78269	-0.70607
C4	-3.95397	-2.67214	0.296973
C5	-3.43017	-2.56692	1.56448
C6	-6.64006	1.874879	-1.51438
C7	-6.32639	1.419917	-2.77306
C8	-4.96281	1.238416	-3.10945
N9	-3.96773	1.499744	-2.28443
H10	-3.88276	-1.85054	-1.7235
H11	-4.69429	-3.42663	0.051357
H12	-3.74238	-3.24152	2.357564
O13	-1.83684	-1.25398	-3.41193
H14	-4.68565	0.856455	-4.09029
H15	-0.19881	-0.54424	-2.07272
C22	-0.76065	-1.88003	-3.3502
O23	0.23681	-1.5699	-2.61718
C24	-0.56883	-3.13103	-4.22486
F25	-0.13449	-4.16382	-3.48181
F26	-1.71346	-3.49625	-4.81811

F27	0.342804	-2.88359	-5.18143
C28	-4.25444	1.977899	-1.03456
C29	-5.60078	2.166104	-0.59293
C30	-5.84403	2.616706	0.730318
C31	-4.78632	2.873575	1.57114
C32	-3.45328	2.711009	1.122148
C33	-3.1666	2.268624	-0.15608
H34	-6.8698	2.751799	1.063888
H35	-4.96684	3.216596	2.585936
H36	-2.63555	2.945251	1.797437
C37	-2.08016	-0.70466	0.774857
C38	-2.45961	-1.57013	1.841853
C39	-1.83855	-1.41396	3.107294
C40	-0.88252	-0.44113	3.28586
C41	-0.52204	0.420772	2.223625
C42	-1.10778	0.315075	0.972934
H43	-2.11995	-2.07709	3.920578
H44	-0.3993	-0.3232	4.251496
H45	0.220515	1.194137	2.396993
H46	-7.09725	1.190502	-3.5021
H47	-7.67467	2.013382	-1.2098
C48	-1.74136	2.200521	-0.65543
C49	-0.75116	1.266188	-0.13371
C50	0.641783	1.635842	-0.21994
C51	1.024756	2.81941	-0.77393
C52	0.060554	3.736041	-1.26802
C53	-1.26819	3.446203	-1.20953
H54	1.399956	0.964837	0.1699
F49	2.322261	3.160431	-0.86374
F50	0.499617	4.89972	-1.7783
H57	-1.98265	4.179301	-1.56823
C58	-0.69441	1.494575	-3.52079
H59	-0.60736	0.822238	-4.38354
H60	-1.29456	2.360543	-3.82085
H61	0.305809	1.838235	-3.23954

Table S147. $[\text{Rh}^{\text{I-III}}(\text{bisq}^{\text{F2}})(\text{H}_{\text{eq}}\cdots\text{TFA}_{\text{ax}})(\text{Me}_{\text{eq}})]^{\ddagger}$
thermodynamic values

Temp	298.15	498.15
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E_{gas}	-1907.81	-1907.81
E_{solv}	-1907.83	-1907.83
G	-1907.48	-1907.54
ZPE	243.599	243.599
H_{vib}	17.957	47.561
S_{trans}	45.059	47.609
S_{rot}	37.160	38.690
S_{vib}	115.009	189.648
solv	-11.8	-11.8

Table S148. [Rh^{I-III}(bisq^{F2})(H_{eq}...TFA_{eq})(Me_{ax})][‡]
Cartesian coordinates

Atom	x	y	z
Rh1	-1.52889	0.280437	-2.02766
N2	-2.38781	-1.12019	0.472673
C3	-3.13625	-2.18278	0.259046
C4	-3.61009	-3.0326	1.287505
C5	-3.26451	-2.74489	2.585355
C6	-6.15553	1.745856	-1.97515
C7	-5.63535	1.204371	-3.12647
C8	-4.27508	0.838635	-3.16573
N9	-3.44491	1.016139	-2.14065
H10	-3.37967	-2.39391	-0.78083
H11	-4.22581	-3.89197	1.040774
H12	-3.59763	-3.37272	3.40841
H13	-3.8515	0.366828	-4.04323
O14	0.503192	-0.46364	-1.99107
C15	1.085604	-0.03572	-3.00466
O16	0.553113	0.71332	-3.89725
C17	2.576846	-0.36354	-3.17627
F18	2.968184	-0.26178	-4.45258
F19	3.298869	0.502966	-2.43852
F20	2.843836	-1.60564	-2.74789
H21	-0.55835	0.815428	-3.4614
C28	-3.92307	1.626968	-0.99671
C29	-5.30263	1.969348	-0.8653
C30	-5.7674	2.512787	0.359573
C31	-4.88927	2.726315	1.395787
C32	-3.51511	2.441589	1.238141

C33	-3.01203	1.905376	0.064612
H34	-6.82158	2.756607	0.459868
H35	-5.2421	3.141189	2.335522
H36	-2.83209	2.665985	2.050292
C37	-2.03678	-0.81049	1.752791
C38	-2.45189	-1.61525	2.861843
C39	-2.03858	-1.27853	4.175898
C40	-1.23099	-0.18541	4.382893
C41	-0.81757	0.612047	3.292469
C42	-1.20338	0.333088	1.989901
H43	-2.36468	-1.89858	5.007297
H44	-0.90798	0.075216	5.386681
H45	-0.187	1.476813	3.478402
H46	-6.25266	1.031825	-4.00179
H47	-7.20702	2.009887	-1.90062
C48	-1.54169	1.735177	-0.13769
C49	-0.69122	1.169073	0.871546
C50	0.679895	1.396334	0.810633
C51	1.241475	2.17854	-0.20252
C52	0.441647	2.726894	-1.18149
C53	-0.94268	2.491811	-1.18577
H54	1.348327	0.93748	1.530912
F49	2.568075	2.38979	-0.22515
F50	0.983511	3.495976	-2.13883
H57	-1.54931	3.09749	-1.84863
C58	-2.00264	-1.29438	-3.27985
H59	-2.00561	-1.01515	-4.34177
H60	-1.26945	-2.09634	-3.13417
H61	-2.99927	-1.68035	-3.02545

Table S149. [Rh^{I-III}(bisq^{F2})(H_{eq}...TFA_{eq})(Me_{ax})][‡]
thermodynamic values

Temp	298.15	498.15
E_{gas}	-1907.82	-1907.82
E_{solv}	-1907.83	-1907.83
G	-1907.49	-1907.55
ZPE	244.053	244.053
H_{vib}	17.921	47.448
S_{trans}	45.059	47.609

S_{rot}	37.130	38.660
S_{vib}	114.914	189.358
solv	-11.3	-11.3

Table S150.

[Rh^{III}(bisq^{F2})(Me_{ax}...H...TFA_{eq})(TFA_{eq})]⁺⁺ Cartesian coordinates

Atom	x	y	z
Rh1	-2.75128	0.343959	-1.44077
N2	-1.60124	-0.68017	0.051748
C3	-1.86653	-1.95933	0.303146
C4	-1.08656	-2.76919	1.143707
C5	0.032769	-2.2244	1.724302
C11	-6.27576	-0.33769	1.876911
C12	-6.48969	-0.81349	0.603751
C13	-5.53506	-0.5509	-0.39929
N14	-4.44504	0.175091	-0.18091
H15	-2.72976	-2.38006	-0.19409
H16	-1.36647	-3.80565	1.293441
H17	0.686413	-2.82179	2.35336
H23	-5.66118	-0.96539	-1.39066
O28	-1.00973	0.686169	-2.51766
C29	-0.45287	-0.32066	-3.04528
O30	-0.88371	-1.49249	-3.01637
C31	0.914379	-0.06684	-3.72151
F32	0.98328	-0.70243	-4.88887
F33	1.128021	1.239178	-3.91452
F34	1.877712	-0.53922	-2.90642
O35	-3.838	1.424566	-2.77763
C36	-3.61007	1.324028	-4.06192
O37	-2.91587	0.522768	-4.65662
C38	-4.37861	2.437146	-4.8256
F39	-4.26968	2.281115	-6.14301
F40	-5.68392	2.431877	-4.4966
F41	-3.86835	3.642924	-4.49189
H42	-2.20324	-1.33189	-2.63609
C43	-3.49742	-1.53056	-2.60735
H44	-3.20346	-2.06198	-3.52354
H45	-3.79333	-2.25874	-1.85447

H46	-4.3236	-0.90758	-2.93253
C41	0.342931	-0.86133	1.505307
C42	-0.52659	-0.07888	0.678305
C35	-0.24851	1.313141	0.508145
C44	0.896284	1.839122	1.091402
C45	1.775704	1.056796	1.866814
C46	1.495059	-0.26935	2.084227
H50	1.104843	2.897562	0.969562
H51	2.658689	1.51446	2.30059
H52	2.147271	-0.88628	2.695047
C47	-4.27281	0.771128	1.050667
C48	-5.14697	0.478406	2.137212
C49	-4.86017	1.03272	3.411899
C50	-3.77732	1.865404	3.577763
C51	-2.97656	2.226382	2.469317
C52	-3.21712	1.703652	1.212147
H55	-5.51414	0.798804	4.246337
H56	-3.55858	2.290117	4.552244
H57	-2.1854	2.958272	2.600813
H53	-6.96875	-0.56432	2.682211
H54	-7.35987	-1.41146	0.357634
C55	-1.14125	2.236928	-0.23419
C56	-2.55576	2.270855	-0.01352
C57	-3.32913	3.269627	-0.6861
C58	-2.74115	4.153261	-1.55174
C59	-1.35204	4.08827	-1.77483
C60	-0.56698	3.14914	-1.13363
H63	-4.39512	3.345108	-0.50559
F60	-3.44765	5.089157	-2.17453
F61	-0.80879	4.940529	-2.62976
H66	0.486261	3.10018	-1.38293

Table S151.

[Rh^{III}(bisq^{F2})(Me_{ax}...H...TFA_{eq})(TFA_{eq})]⁺⁺
thermodynamic values

Temp	298.15	498.15
E_{gas}	-2433.75	-2433.75
E_{solv}	-2433.83	-2433.83
G	-2433.45	-2433.53

ZPE	264.606	264.606
H_{vib}	21.853	56.770
S_{trans}	45.573	48.123
S_{rot}	37.770	39.300
S_{vib}	140.822	228.938
solv	-47.7	-47.7

Table S152.

[Rh^{III}(bisq^{F2})(Me_{eq}...H...TFA_{ax})(TFA_{eq})]⁺⁺ Cartesian coordinates

Atom	x	y	z
Rh1	-1.45754	0.099041	-1.59367
N2	-1.83373	-1.35737	-0.09268
C3	-1.91324	-2.65722	-0.34344
C4	-2.35151	-3.57965	0.629726
C5	-2.74138	-3.12203	1.868076
C11	-6.22154	1.378987	-1.41131
C12	-5.77492	0.206309	-1.96785
C13	-4.39662	-0.06424	-1.95282
N14	-3.48948	0.750256	-1.41523
H15	-1.65228	-2.97524	-1.34547
H16	-2.39387	-4.6325	0.374517
H17	-3.11663	-3.80761	2.622538
H22	-4.01435	-0.96827	-2.40959
O27	0.396512	-0.75519	-1.69086
C28	1.467636	-0.13056	-2.09178
O29	1.577903	0.995499	-2.54139
C30	2.721664	-1.00996	-1.83725
F31	2.918233	-1.09957	-0.49965
F32	2.559178	-2.2543	-2.31861
F33	3.809401	-0.47567	-2.38784
H34	-0.56698	1.865416	-4.08526
H35	-0.82876	0.49975	-3.70671
O36	-1.99278	-1.38194	-2.93287
C37	-1.39548	-1.40533	-4.0549
O38	-0.68485	-0.49224	-4.51728
C39	-1.63102	-2.69017	-4.88072
F40	-0.92643	-2.68235	-6.00397
F41	-1.28339	-3.75557	-4.14104

F42	-2.93904	-2.77928	-5.17387
C43	-1.17834	1.717656	-3.18022
H44	-2.19364	2.039051	-3.41226
H45	-0.67169	2.369807	-2.48103
C41	-5.29522	2.271629	-0.82163
C42	-3.90424	1.923263	-0.81143
C35	-2.97917	2.825803	-0.19632
C44	-3.45564	4.022571	0.323364
C45	-4.82083	4.368757	0.2943
C46	-5.72807	3.500465	-0.26035
H50	-2.75212	4.701596	0.795622
H51	-5.14505	5.312326	0.720776
H52	-6.78696	3.739775	-0.2862
C47	-2.12594	-0.88132	1.157997
C48	-2.64026	-1.74037	2.170717
C49	-3.00638	-1.17348	3.418562
C50	-2.8385	0.17484	3.641322
C51	-2.25501	1.000793	2.651664
C52	-1.88699	0.488039	1.420304
H55	-3.41131	-1.81822	4.192876
H56	-3.1181	0.608513	4.596122
H57	-2.0608	2.04514	2.878236
H53	-7.2762	1.638897	-1.41712
H54	-6.44981	-0.50581	-2.42887
C55	-1.52941	2.540623	-0.07197
C56	-1.05421	1.301341	0.461503
C57	0.360243	1.112087	0.590942
C58	1.241814	2.098162	0.224827
C59	0.752375	3.324244	-0.25849
C60	-0.60765	3.540339	-0.41613
H63	0.75149	0.19045	1.006939
F60	2.553832	1.927209	0.33794
F61	1.617985	4.2673	-0.58963
H66	-0.93455	4.481018	-0.84533

Table S153.

[Rh^{III}(bisq^{F2})(Me_{eq}...H...TFA_{ax})(TFA_{eq})]⁺⁺
thermodynamic values

Temp	298.15	498.15
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E_{gas}	-2433.75	-2433.75
E_{solv}	-2433.83	-2433.83
G	-2433.45	-2433.52
ZPE	264.596	264.596
H_{vib}	21.975	56.854
S_{trans}	45.573	48.123
S_{rot}	37.902	39.432
S_{vib}	142.175	230.191
solv	-45.2	-45.2

Table S154.

[Rh^{III}(bisq^{F2})(Me_{eq}...H...TFA_{eq})(TFA_{ax})]⁺⁺ Cartesian coordinates

Atom	x	y	z
Rh1	-2.55166	0.07228	-1.44053
N2	-1.43324	-1.15529	-0.10572
C3	-1.63337	-2.46855	-0.09044
C4	-0.97868	-3.32699	0.8131
C5	-0.10399	-2.79408	1.728776
C11	-5.86467	0.101639	2.14905
C12	-5.94691	-0.80532	1.119644
C13	-5.00642	-0.74391	0.074389
N14	-4.04401	0.172449	0.029772
H15	-2.33613	-2.85497	-0.81798
H16	-1.18266	-4.39078	0.768402
H17	0.41032	-3.42629	2.446983
H23	-5.02062	-1.4607	-0.73814
O28	-0.9907	-0.26293	-2.7663
C29	-0.9943	0.434043	-3.82349
O30	-1.83752	1.310068	-4.1155
C31	0.219601	0.233645	-4.75657
F32	1.243002	0.958773	-4.25031
F33	0.585704	-1.04932	-4.79502
F34	-0.03968	0.658965	-5.98848
H35	-4.15633	1.76478	-3.6696
H36	-2.84102	1.176804	-3.24665
O37	-3.42878	-1.61466	-2.10649
C38	-3.52429	-1.95967	-3.37304
O39	-3.19594	-1.35513	-4.36616

C40	-4.19573	-3.36113	-3.44429
F41	-4.33043	-3.77134	-4.6979
F42	-3.45318	-4.26388	-2.76564
F43	-5.41558	-3.3136	-2.86491
C44	-4.09577	1.208215	-2.72178
H45	-4.77606	0.368664	-2.83489
H46	-4.43498	1.896167	-1.95295
C41	-3.95215	1.123742	1.022326
C42	-4.85952	1.099473	2.127111
C43	-4.74141	2.079539	3.14482
C36	-3.77735	3.056208	3.058802
C45	-2.9093	3.09523	1.94638
C46	-2.97597	2.150135	0.935665
H49	-5.43222	2.05055	3.982198
H50	-3.68835	3.811633	3.832738
H51	-2.17562	3.892898	1.874051
C48	-0.53435	-0.58924	0.768589
C49	0.147114	-1.40026	1.728914
C50	1.067042	-0.79653	2.622971
C51	1.319027	0.553117	2.552514
C52	0.670632	1.341035	1.577517
C53	-0.249	0.797793	0.695175
H55	1.577641	-1.42164	3.349479
H56	2.029353	1.017305	3.228856
H57	0.906818	2.399004	1.508026
H53	-6.71047	-1.57447	1.094822
H54	-6.56522	0.072293	2.978774
C55	-0.81524	1.684077	-0.37108
C56	-2.08594	2.315943	-0.26083
C57	-2.38218	3.412304	-1.11895
C58	-1.47244	3.838727	-2.05417
C59	-0.22305	3.1958	-2.17677
C60	0.10093	2.143883	-1.35408
H63	-3.32234	3.944303	-1.0243
F60	-1.74425	4.86144	-2.85772
F61	0.62823	3.633484	-3.09605
H66	1.073127	1.676892	-1.45945

Table S155.

$$[\text{Rh}^{\text{III}}(\text{bisq}^{\text{F2}})(\text{Me}_{\text{eq}}\cdots\text{H}\cdots\text{TFA}_{\text{eq}})(\text{TFA}_{\text{ax}})]^{+\ddagger}$$

thermodynamic values

Temp	298.15	498.15
E _{gas}	-2433.76	-2433.76
E _{solv}	-2433.83	-2433.83
G	-2433.46	-2433.53
ZPE	264.768	264.768
H _{vib}	21.875	56.742
S _{trans}	45.573	48.123
S _{rot}	37.880	39.410
S _{vib}	141.514	229.504
solv	-43.9	-43.9

Table S156. $[\text{Rh}^{\text{III}}(\text{bisq}^{\text{F2}})(\text{Me}_{\text{ax}}\cdots\text{TFA}_{\text{eq}})(\text{TFA}_{\text{eq}})]^{\ddagger}$

Cartesian coordinates

Atom	x	y	z
Rh1	-1.71156	0.220847	-1.88418
N2	-2.39169	-0.82996	-0.16356
C3	-3.23131	-1.84178	-0.3547
C4	-3.59945	-2.76403	0.64054
C5	-3.04122	-2.63387	1.887553
C6	-6.3885	1.514302	-1.81879
C7	-5.84957	0.97047	-2.95981
C8	-4.45904	0.74763	-3.02168
N9	-3.62351	1.074664	-2.03766
H10	-3.632	-1.94808	-1.35651
H11	-4.28574	-3.56776	0.396938
H12	-3.26104	-3.34272	2.681358
H13	-4.00565	0.272713	-3.88459
O14	0.136229	-0.62251	-1.4337
C15	1.048825	-1.03574	-2.2335
O16	1.026911	-1.22336	-3.44674
C17	2.355534	-1.35582	-1.45312
F18	3.339105	-1.77391	-2.26001
F19	2.809694	-0.26494	-0.78732
F20	2.139683	-2.32364	-0.53176
O21	-0.93779	1.266457	-3.51072

C22	-1.3256	0.923652	-4.64609
O23	-2.08772	-0.03584	-4.96522
C24	-0.86935	1.797358	-5.83706
F25	-0.37208	1.033994	-6.82142
F26	-1.93317	2.472862	-6.32677
F27	0.059295	2.690218	-5.48049
C28	-4.12064	1.741688	-0.93305
C29	-5.5305	1.916156	-0.76445
C30	-6.02735	2.49121	0.434185
C31	-5.15629	2.907769	1.412204
C32	-3.76175	2.817341	1.202548
C33	-3.22707	2.263533	0.052429
H34	-7.10147	2.601673	0.556047
H35	-5.53145	3.345816	2.332361
H36	-3.08406	3.224796	1.946885
C37	-1.88457	-0.61482	1.103282
C38	-2.16792	-1.5524	2.15354
C39	-1.5843	-1.39175	3.436113
C40	-0.75962	-0.32369	3.686317
C41	-0.5257	0.63043	2.67543
C42	-1.07043	0.527319	1.402661
H43	-1.80566	-2.12536	4.206232
H44	-0.30239	-0.19357	4.662582
H45	0.09038	1.495804	2.899521
H46	-6.46964	0.6768	-3.80021
H47	-7.46109	1.654169	-1.71278
C48	-1.75432	2.393605	-0.20599
C49	-0.76085	1.623827	0.443232
C50	0.592238	1.941193	0.235802
C51	0.95336	2.992062	-0.58751
C52	-0.02477	3.762599	-1.21133
C53	-1.36305	3.476936	-1.01435
H54	1.375481	1.32439	0.658723
F55	2.245821	3.281116	-0.79676
F56	0.343122	4.786587	-1.99479
H57	-2.10415	4.096357	-1.50755
C58	-1.97758	-1.70924	-3.86865
H59	-2.43467	-2.06274	-4.78461
H60	-0.89638	-1.78637	-3.79792
H61	-2.55245	-1.92134	-2.97872

Table S157. $[\text{Rh}^{\text{III}}(\text{bisq}^{\text{F2}})(\text{Me}_{\text{ax}}\cdots\text{TFA}_{\text{eq}})(\text{TFA}_{\text{eq}})]^{\ddagger}$
thermodynamic values

Temp	298.15	498.15
E_{gas}	-2433.35	-2433.35
E_{solv}	-2433.38	-2433.38
G	-2433.02	-2433.09
ZPE	258.363	258.363
H_{vib}	22.259	56.939
S_{trans}	45.569	48.119
S_{rot}	37.892	39.422
S_{vib}	145.686	233.230
S_{olv}	-18.7	-18.7

Table S158. $[\text{Rh}^{\text{III}}(\text{bisq}^{\text{F2}})(\text{Me}_{\text{eq}}\cdots\text{TFA}_{\text{ax}})(\text{TFA}_{\text{eq}})]^{\ddagger}$
Cartesian coordinates

Atom	x	y	z
Rh1	-1.43729	0.737129	-2.24333
N2	-2.14792	-1.04417	-0.0848
C3	-2.77152	-2.13818	-0.47369
C4	-3.18764	-3.15909	0.414958
C5	-2.91662	-3.01401	1.753773
C6	-6.17445	1.816893	-2.05346
C7	-5.6319	1.429832	-3.25596
C8	-4.24539	1.189122	-3.34713
N9	-3.42294	1.32959	-2.31185
H10	-2.94383	-2.23302	-1.54412
H11	-3.7012	-4.03501	0.030735
H12	-3.21165	-3.77478	2.472745
O13	-1.81803	-0.95721	-3.43767
H14	-3.79374	0.881565	-4.28231
O15	0.486983	0.074642	-1.92034
C16	1.290976	-0.42384	-2.78791
O17	1.197323	-0.50486	-4.00963
C18	2.561508	-0.98362	-2.08905
F19	3.494481	-1.36221	-2.97294
F20	3.117781	-0.05484	-1.27664
F21	2.255079	-2.056	-1.32642

C22	-1.9357	-0.7752	-4.66876
O23	-1.84567	0.297427	-5.32275
C24	-2.35572	-2.00424	-5.51001
F25	-1.61641	-2.10822	-6.61974
F26	-2.25363	-3.14667	-4.82015
F27	-3.65037	-1.85468	-5.87581
C28	-3.93061	1.773031	-1.10941
C29	-5.32561	2.003944	-0.93366
C30	-5.79789	2.398099	0.344538
C31	-4.91176	2.569706	1.38305
C32	-3.52512	2.380295	1.185368
C33	-3.01947	1.988852	-0.0414
H34	-6.86308	2.559495	0.485875
H35	-5.27148	2.869866	2.362834
H36	-2.84286	2.554982	2.009997
C37	-1.85915	-0.87919	1.236666
C38	-2.22649	-1.86116	2.21077
C39	-1.88459	-1.66948	3.573783
C40	-1.18295	-0.551	3.95725
C41	-0.80808	0.417361	2.999336
C42	-1.13371	0.286514	1.658372
H43	-2.17816	-2.42158	4.301624
H44	-0.91375	-0.40364	4.999204
H45	-0.25629	1.295718	3.322533
H46	-6.24736	1.291596	-4.13841
H47	-7.24223	1.98706	-1.94779
C48	-1.54941	1.887758	-0.30007
C49	-0.66378	1.293284	0.673727
C50	0.678766	1.622602	0.650353
C51	1.200309	2.52655	-0.29113
C52	0.38218	3.093428	-1.23354
C53	-0.99489	2.77881	-1.27661
H54	1.378936	1.139754	1.323269
F55	2.509003	2.814112	-0.2731
F56	0.873612	3.948885	-2.14678
H57	-1.64054	3.462906	-1.81835
C58	-0.66011	1.852994	-4.67975
H59	0.224254	1.225062	-4.64477
H60	-1.00815	2.182185	-5.64876
H61	-0.82059	2.55264	-3.87274

Table S159. $[\text{Rh}^{\text{III}}(\text{bisq}^{\text{F2}})(\text{Me}_{\text{eq}}\cdots\text{TFA}_{\text{ax}})(\text{TFA}_{\text{eq}})]^{\ddagger}$
thermodynamic values

Temp	298.15	498.15
E_{gas}	-2433.35	-2433.35
E_{solv}	-2433.37	-2433.37
G	-2433.01	-2433.08
ZPE	258.061	258.061
H_{vib}	22.393	57.105
S_{trans}	45.569	48.119
S_{rot}	37.956	39.486
S_{vib}	146.696	234.321
solv	-16.6	-16.6

Table S160. $[\text{Rh}^{\text{III}}(\text{bisq}^{\text{F2}})(\text{Me}_{\text{eq}}\cdots\text{TFA}_{\text{eq}})(\text{TFA}_{\text{ax}})]^{\ddagger}$
Cartesian coordinates

Atom	x	y	z
Rh1	-1.42453	0.728713	-2.20346
N2	-2.10351	-0.97809	-0.03398
C3	-2.71889	-2.08481	-0.40289
C4	-3.08478	-3.11128	0.50163
C5	-2.77622	-2.95837	1.830857
C6	-6.12533	1.859588	-2.05012
C7	-5.58892	1.415816	-3.23687
C8	-4.20465	1.159425	-3.3189
N9	-3.3838	1.36836	-2.29701
H10	-2.91923	-2.18602	-1.46726
H11	-3.59036	-3.99868	0.134101
H12	-3.03275	-3.72351	2.559749
O13	-2.08627	-0.84697	-3.41232
H14	-3.75633	0.735832	-4.20998
O15	0.444996	-0.12094	-1.95267
C16	1.388334	0.30306	-2.66184
O17	1.384032	1.208485	-3.52977
C18	2.767286	-0.3205	-2.33238
F19	3.627462	-0.20799	-3.34981
F20	3.288932	0.328335	-1.26523
F21	2.653608	-1.61664	-2.01279

C22	-1.44029	-1.54714	-4.27933
O23	-0.35308	-1.35442	-4.8065
C24	-2.28107	-2.78557	-4.70282
F25	-1.62675	-3.57724	-5.55914
F26	-2.62768	-3.53747	-3.62974
F27	-3.4311	-2.38942	-5.30032
C28	-3.88366	1.844616	-1.10777
C29	-5.27764	2.074644	-0.93374
C30	-5.74532	2.47289	0.34481
C31	-4.85556	2.636311	1.381765
C32	-3.46845	2.440778	1.185485
C33	-2.96499	2.053502	-0.0433
H34	-6.80984	2.632841	0.491359
H35	-5.21403	2.92969	2.363971
H36	-2.78675	2.601727	2.013861
C37	-1.77492	-0.8059	1.278256
C38	-2.09529	-1.79142	2.265112
C39	-1.7158	-1.59126	3.616696
C40	-1.02346	-0.46016	3.978746
C41	-0.69041	0.510067	3.00819
C42	-1.04966	0.36876	1.676294
H43	-1.9736	-2.34753	4.353453
H44	-0.72681	-0.30562	5.012039
H45	-0.14145	1.396989	3.312036
H46	-6.21046	1.235524	-4.10729
H47	-7.19267	2.037475	-1.95082
C48	-1.49771	1.928719	-0.31438
C49	-0.60105	1.368044	0.674607
C50	0.734106	1.723441	0.64654
C51	1.24037	2.627908	-0.3073
C52	0.422792	3.139501	-1.27919
C53	-0.94747	2.78315	-1.32827
H54	1.441138	1.270974	1.333373
F55	2.539015	2.963312	-0.26759
F56	0.894257	4.007723	-2.18633
H57	-1.59596	3.447923	-1.88998
C58	-0.31285	1.7829	-4.51192
H59	-0.32734	0.836608	-5.03775
H60	-1.25876	2.181941	-4.1718
H61	0.406446	2.526043	-4.8252

Table S161. $[\text{Rh}^{\text{III}}(\text{bisq}^{\text{F2}})(\text{Me}_{\text{eq}}\cdots\text{TFA}_{\text{eq}})(\text{TFA}_{\text{ax}})]^{\ddagger}$
thermodynamic values

Temp	298.15	498.15
E_{gas}	-2433.35	-2433.35
E_{solv}	-2433.37	-2433.37
G	-2433.01	-2433.08
ZPE	258.098	258.098
H_{vib}	22.331	57.053
S_{trans}	45.569	48.119
S_{rot}	37.933	39.463
S_{vib}	146.223	233.876
solv	-16.4	-16.4

Table S162. $[\text{Rh}^{\text{III}}(\text{bisq}^{\text{F2}})(\text{Me}_{\text{ax}}\cdots\text{TFA})(\text{TFA})_2]^{\ddagger}$
Cartesian coordinates

Atom	x	y	z
Rh1	-1.49397	0.379553	-2.0338
N2	-2.29122	-0.84722	-0.5043
C3	-3.06988	-1.87637	-0.83153
C4	-3.45482	-2.88654	0.071999
C5	-2.9913	-2.83314	1.360568
C6	-6.20544	1.40479	-2.42296
C7	-5.48068	1.115777	-3.55426
C8	-4.07703	0.998093	-3.46715
N9	-3.40835	1.186361	-2.33041
H10	-3.37969	-1.97074	-1.8647
H11	-4.06981	-3.69957	-0.29799
H12	-3.2222	-3.61354	2.081673
H13	-3.46394	0.741213	-4.32734
O14	0.33872	-0.4591	-1.50024
C15	1.312847	-0.72964	-2.29276
O16	1.382862	-0.76736	-3.51269
C17	2.582887	-1.08504	-1.46254
F18	3.657688	-1.31644	-2.23552
F19	2.920667	-0.08605	-0.60387
F20	2.385826	-2.19536	-0.70803
O21	-0.54861	1.690255	-3.32906

C22	-0.81484	1.873542	-4.56028
O23	-1.64496	1.335839	-5.29863
C24	0.047619	2.995233	-5.20539
F25	-0.756	3.989431	-5.6658
F26	0.928472	3.56361	-4.36079
F27	0.743164	2.527305	-6.263
C28	-4.09334	1.649871	-1.22309
C29	-5.52157	1.692096	-1.21386
C30	-6.20042	2.040309	-0.01715
C31	-5.49031	2.386057	1.10798
C32	-4.07971	2.457696	1.059245
C33	-3.37217	2.116569	-0.07982
H34	-7.2878	2.039324	-0.01414
H35	-6.00908	2.650731	2.025407
H36	-3.53154	2.82314	1.922875
C37	-1.88961	-0.70974	0.812126
C38	-2.19285	-1.73524	1.767655
C39	-1.70168	-1.64657	3.094332
C40	-0.95209	-0.56437	3.482482
C41	-0.70953	0.477592	2.565981
C42	-1.16614	0.445795	1.255492
H43	-1.93294	-2.45007	3.789234
H44	-0.56557	-0.49115	4.495272
H45	-0.1629	1.356287	2.894961
H46	-5.96375	0.928775	-4.50764
H47	-7.29212	1.438035	-2.4395
C48	-1.90869	2.427827	-0.17038
C49	-0.88738	1.650639	0.422232
C50	0.443708	2.091963	0.332416
C51	0.753023	3.265287	-0.33202
C52	-0.25315	4.036281	-0.90268
C53	-1.57258	3.63055	-0.8112
H54	1.253274	1.477249	0.706587
F55	2.030222	3.674965	-0.43269
F56	0.063895	5.182835	-1.52903
H57	-2.33862	4.243881	-1.27325
C58	-1.72858	-1.53097	-3.7132
H59	-1.03771	-1.06562	-4.39763
H60	-1.33514	-2.12367	-2.90509
H61	-2.76751	-1.25804	-3.72724

O62	-2.04656	-3.05872	-4.8
C63	-3.07733	-3.70788	-4.41772
O64	-3.86022	-3.496	-3.48701
C65	-3.39182	-4.92991	-5.33094
F66	-2.30099	-5.44488	-5.92759
F67	-3.978	-5.92671	-4.63431
F68	-4.25584	-4.56728	-6.31102

Table S163. $[\text{Rh}^{\text{III}}(\text{bisq}^{\text{F2}})(\text{Me}_{\text{ax}}\cdots\text{TFA})(\text{TFA})_2]^{+}$
thermodynamic values

Temp	298.15	498.15
E_{gas}	-2959.66	-2959.66
E_{solv}	-2959.74	-2959.74
G	-2959.36	-2959.45
ZPE	276.089	276.089
H_{vib}	26.607	66.542
S_{trans}	46.008	48.558
S_{rot}	39.027	40.558
S_{vib}	182.624	284.516
solv	-48.0	-48.0

Table S164. $[\text{Rh}^{\text{III}}(\text{bisq}^{\text{F2}})(\text{Me}_{\text{ax}}\cdots\text{TFAH})(\text{TFA})_2]^{+}$
Cartesian coordinates

Atom	x	y	z
Rh1	-1.95116	0.146179	-1.80875
N2	-2.59162	-0.8771	-0.06911
C3	-3.48579	-1.85338	-0.2032
C4	-3.84306	-2.74559	0.82318
C5	-3.2195	-2.62711	2.039258
C6	-6.5106	1.665333	-1.58656
C7	-6.00288	1.193417	-2.77281
C8	-4.62272	0.921851	-2.8715
N9	-3.77331	1.135436	-1.86793
H10	-3.93098	-1.96012	-1.18327
H11	-4.57601	-3.51962	0.624222
H12	-3.4315	-3.31512	2.853021
H13	-4.18368	0.532006	-3.78346
O14	-0.02325	-0.91377	-1.68651

C15	0.970743	-1.12231	-2.38024
O16	1.074939	-1.58479	-3.57812
C17	2.356472	-0.79305	-1.76788
F18	3.334838	-1.5358	-2.2935
F19	2.639906	0.503705	-1.97725
F20	2.331047	-1.00608	-0.43797
O21	-1.04075	1.219166	-3.31935
C22	-1.48855	1.482575	-4.4923
O23	-2.48855	1.053769	-5.06675
C24	-0.56389	2.490592	-5.22783
F25	-1.04845	2.827353	-6.43089
F26	-0.42718	3.625386	-4.50527
F27	0.667569	1.96831	-5.40575
C28	-4.2266	1.769377	-0.72657
C29	-5.62571	1.977886	-0.5239
C30	-6.07894	2.514512	0.708827
C31	-5.17659	2.878961	1.679106
C32	-3.78962	2.777833	1.427439
C33	-3.29811	2.249224	0.246761
H34	-7.14684	2.645649	0.860655
H35	-5.52116	3.29126	2.622695
H36	-3.0855	3.159586	2.16092
C37	-2.0129	-0.67072	1.172934
C38	-2.28598	-1.58373	2.246792
C39	-1.63389	-1.43854	3.497302
C40	-0.75023	-0.40867	3.698186
C41	-0.52484	0.524174	2.66673
C42	-1.13498	0.4351	1.422918
H43	-1.85142	-2.15476	4.284544
H44	-0.2417	-0.29035	4.650153
H45	0.135132	1.366094	2.852244
H46	-6.64001	0.98968	-3.62653
H47	-7.57706	1.828956	-1.45571
C48	-1.83975	2.373201	-0.07566
C49	-0.8379	1.529783	0.454107
C50	0.509918	1.811083	0.16963
C51	0.853016	2.881787	-0.63678
C52	-0.13504	3.712048	-1.15913
C53	-1.46627	3.470314	-0.86859
H54	1.298523	1.166482	0.538704

F55	2.138583	3.132613	-0.92089
F56	0.21531	4.751764	-1.92501
H57	-2.21572	4.136388	-1.28226
C58	-2.55359	-1.69266	-3.41894
H59	-2.20486	-0.96907	-4.13719
H60	-1.87897	-2.25998	-2.8
H61	-3.60921	-1.71061	-3.19507
O62	-2.74427	-3.04641	-4.69591
C63	-1.64561	-3.26986	-5.29176
O64	-0.51335	-2.81207	-5.06103
C65	-1.74281	-4.24711	-6.49391
F66	-2.96518	-4.78376	-6.62068
F67	-1.44998	-3.59546	-7.63363
F68	-0.85912	-5.25116	-6.34571
H69	0.246178	-1.95688	-4.06685

Table S165. $[\text{Rh}^{\text{III}}(\text{bisq}^{\text{F2}})(\text{Me}_{\text{ax}}\cdots\text{TFAH})(\text{TFA})_2]^{\ddagger}$
thermodynamic values

Temp	298.15	498.15
E_{gas}	-2960.15	-2960.15
E_{solv}	-2960.18	-2960.18
G	-2959.79	-2959.87
ZPE	284.220	284.220
H_{vib}	26.973	67.420
S_{trans}	46.012	48.562
S_{rot}	38.963	40.493
S_{vib}	180.149	282.317
solv	-20.8	-20.8

Table S166. $[\text{Rh}^{\text{III}}(\text{bisq}^{\text{F2}})(\text{Me}_{\text{ax}}\cdots\text{TFA})(\text{TFA}_{\text{eq}})(\text{TFAH}_{\text{eq}})]^{\ddagger}$ Cartesian
coordinates

Atom	x	y	z
Rh1	-1.07007	0.676949	-1.82157
N2	-1.63456	-0.91701	-0.58539
C3	-1.85082	-2.12367	-1.10258
C4	-2.54188	-3.1425	-0.41414
C5	-3.05217	-2.87733	0.831512

C6	-5.50561	2.72529	-1.50206
C7	-5.26977	1.579805	-2.21707
C8	-3.97428	1.034672	-2.20261
N9	-2.95521	1.547365	-1.51827
H10	-1.52939	-2.31047	-2.12123
H11	-2.69237	-4.09132	-0.91643
H12	-3.64057	-3.61602	1.369331
H13	-3.76375	0.155346	-2.79452
O14	0.775117	-0.39796	-1.99443
C15	1.991092	-0.18225	-2.08591
O16	2.603335	0.876932	-2.45114
C17	2.936421	-1.32039	-1.63656
F18	4.077067	-1.32565	-2.33249
F19	3.231512	-1.13406	-0.33169
F20	2.346113	-2.51418	-1.76665
O21	-0.80196	2.354169	-3.07635
C22	0.193001	3.040178	-3.41916
O23	1.41848	2.825277	-3.28379
C24	-0.18401	4.405687	-4.04848
F25	-0.4726	5.275659	-3.04581
F26	0.811365	4.926332	-4.77175
F27	-1.27122	4.309507	-4.8293
H28	1.97402	1.703823	-2.78626
C29	-3.16919	2.67229	-0.74049
C30	-4.45873	3.303979	-0.74631
C31	-4.68061	4.494228	-0.00888
C32	-3.66505	5.051724	0.725129
C33	-2.40872	4.415622	0.763422
C34	-2.13557	3.244927	0.069912
H35	-5.66593	4.950327	-0.04296
H36	-3.82256	5.966856	1.287512
H37	-1.61956	4.844093	1.373837
C38	-2.01146	-0.6666	0.720597
C39	-2.79608	-1.62152	1.439751
C40	-3.27355	-1.30255	2.736309
C41	-2.9519	-0.09988	3.318229
C42	-2.09328	0.796837	2.64664
C43	-1.60624	0.534782	1.377224
H44	-3.88424	-2.03198	3.261322
H45	-3.31593	0.147285	4.310836

H46	-1.77039	1.703213	3.150428
H47	-6.04023	1.097321	-2.80795
H48	-6.48203	3.201771	-1.50283
C49	-0.76493	2.680053	0.239993
C50	-0.52501	1.420211	0.832126
C51	0.799932	1.027057	1.093777
C52	1.861092	1.854364	0.767696
C53	1.624025	3.098033	0.185134
C54	0.327711	3.509298	-0.07286
H55	1.013367	0.070345	1.558017
F56	3.121188	1.471639	1.013563
F57	2.662007	3.884151	-0.12488
H58	0.173338	4.467379	-0.55704
C59	-1.57613	-0.43087	-3.89012
H60	-1.7985	0.479084	-4.42637
H61	-0.5724	-0.8224	-3.90185
H62	-2.35308	-1.00543	-3.42111
O63	-1.9465	-1.49733	-5.53838
C64	-2.1818	-2.70631	-5.20407
O65	-2.22416	-3.22206	-4.08058
C66	-2.46356	-3.65689	-6.4036
F67	-2.41934	-3.0416	-7.59669
F68	-1.56225	-4.6611	-6.42462
F69	-3.68895	-4.21175	-6.2747

Table S167. $[\text{Rh}^{\text{III}}\text{-(bisq}^{\text{F2}})(\text{Me}_{\text{ax}}\cdots\text{TFA})(\text{TFA}_{\text{eq}})(\text{TFAH}_{\text{eq}})]^{\dagger}$
thermodynamic values

Temp	298.15	498.15
E _{gas}	-2960.16	-2960.16
E _{solv}	-2960.19	-2960.19
G	-2959.80	-2959.88
ZPE	283.673	283.673
H _{vib}	26.409	66.374
S _{trans}	46.012	48.562
S _{rot}	39.055	40.585
S _{vib}	180.428	282.368
solv	-21.3	-21.3

Table S168. $[\text{Rh}^{\text{III}}\text{-(bisq}^{\text{F2}})(\text{Me}_{\text{eq}}\cdots\text{TFA})(\text{TFA})_2]^{\dagger}$
Cartesian coordinates

Atom	x	y	z
Rh1	-1.07235	0.165874	-2.38892
N2	-2.26168	-1.15237	0.395688
C3	-2.99339	-2.24354	0.279751
C4	-3.53427	-2.93567	1.394161
C5	-3.28472	-2.46028	2.657519
C6	-5.7729	1.276249	-2.74849
C7	-5.1438	0.642199	-3.79264
C8	-3.76241	0.375884	-3.70979
N9	-3.03076	0.721292	-2.65745
H10	-3.14953	-2.596	-0.73766
H11	-4.12939	-3.82978	1.233159
H12	-3.67657	-2.96374	3.53907
O13	-1.25046	-1.39208	-3.7774
H14	-3.23886	-0.14353	-4.50332
O15	0.732692	-0.65381	-1.83353
C16	1.886138	-0.43867	-2.35098
O17	2.237458	0.3216	-3.24479
C18	2.976789	-1.25639	-1.60151
F19	4.138787	-1.29422	-2.27618
F20	3.232956	-0.68286	-0.39414
F21	2.607018	-2.53186	-1.3628
C22	-2.01199	-2.4138	-3.67553
O23	-2.79065	-2.76086	-2.79104
C24	-1.99077	-3.28045	-4.96681
F25	-3.01417	-2.88537	-5.77484
F26	-0.85808	-3.17405	-5.67986
F27	-2.18048	-4.58596	-4.69497
C28	-3.62388	1.387264	-1.60888
C29	-5.02021	1.670147	-1.61354
C30	-5.59169	2.31843	-0.48945
C31	-4.79819	2.675828	0.575684
C32	-3.40912	2.417242	0.557712
C33	-2.80665	1.778264	-0.51197
H34	-6.6588	2.524988	-0.48747
H35	-5.23357	3.174619	1.437176
H36	-2.79946	2.73303	1.397556

C37	-1.99554	-0.66501	1.637418
C38	-2.48968	-1.29657	2.823265
C39	-2.16545	-0.7655	4.097136
C40	-1.3638	0.347764	4.192623
C41	-0.86749	0.970257	3.026116
C42	-1.16484	0.497771	1.755455
H43	-2.55374	-1.25404	4.988161
H44	-1.10934	0.759512	5.165705
H45	-0.24426	1.854923	3.122523
H46	-5.68605	0.331495	-4.67916
H47	-6.83917	1.483678	-2.77731
C48	-1.32382	1.586246	-0.5856
C49	-0.56497	1.163802	0.56996
C50	0.796962	1.416277	0.604507
C51	1.445962	2.116912	-0.42151
C52	0.742268	2.561012	-1.51192
C53	-0.64139	2.293967	-1.62766
H54	1.405206	1.048695	1.423397
F55	2.763378	2.358445	-0.31959
F56	1.346182	3.280946	-2.46093
H57	-1.18687	2.90629	-2.33886
C58	-0.58588	1.341213	-4.43352
H59	-0.75855	0.479368	-5.06164
H60	-1.37712	2.041798	-4.24241
H61	0.434041	1.54605	-4.14519
O62	-0.29763	2.551097	-6.11149
C63	-0.84994	3.674458	-5.90064
O64	-1.53067	4.080838	-4.94823
C65	-0.6336	4.715053	-7.04373
F66	0.062502	4.240385	-8.09507
F67	-1.82404	5.153921	-7.52228
F68	0.030389	5.802165	-6.58348

Table S169. $[\text{Rh}^{\text{III}}\text{I}(\text{bisq}^{\text{F2}})(\text{Me}_{\text{eq}}\cdots\text{TFA})(\text{TFA})_2]^+$ thermodynamic values

Temp	298.15	498.15
E_{gas}	-2959.66	-2959.66
E_{solv}	-2959.73	-2959.73
G	-2959.36	-2959.44

ZPE	275.729	275.729
H_{vib}	26.730	66.700
S_{trans}	46.008	48.558
S_{rot}	39.148	40.679
S_{vib}	183.059	285.041
solv	-49.5	-49.5

Table S170. $[\text{Rh}^{\text{III}}\text{I}(\text{bisq}^{\text{F2}})(\text{Me}_{\text{eq}}\cdots\text{TFAH})(\text{TFA})_2]^+$ (TFAH H-bonded to TFA_{ax}) Cartesian coordinates

Atom	x	y	z
Rh1	-1.64628	0.998501	-2.2354
N2	-2.43255	-0.88759	-0.15246
C3	-3.16349	-1.90173	-0.57045
C4	-3.55198	-2.98373	0.255083
C5	-3.14777	-2.98632	1.567084
C6	-6.3757	1.947029	-1.74782
C7	-5.89106	1.57981	-2.98215
C8	-4.50664	1.371575	-3.14851
N9	-3.63703	1.530565	-2.15751
H10	-3.45052	-1.88429	-1.61646
H11	-4.14733	-3.79163	-0.15835
H12	-3.41537	-3.79963	2.237453
O13	-2.2033	-0.45642	-3.80664
H14	-4.09739	1.040824	-4.09585
O15	0.350158	0.444948	-2.21961
C16	0.705877	-0.79589	-2.24295
O17	0.032208	-1.80106	-2.43395
C18	2.232346	-0.93647	-1.99021
F19	2.611042	-2.21893	-1.94162
F20	2.93705	-0.32692	-2.96374
F21	2.580839	-0.36021	-0.8135
C22	-1.59256	-1.29134	-4.49153
O23	-0.64357	-1.11886	-5.33351
C24	-2.13361	-2.74146	-4.51644
F25	-1.24313	-3.61722	-4.97466
F26	-2.54865	-3.13929	-3.30657
F27	-3.20922	-2.75251	-5.3413
C28	-4.08925	1.918905	-0.91705
C29	-5.47614	2.123123	-0.66652

C30	-5.88671	2.463986	0.648098
C31	-4.95168	2.594277	1.649207
C32	-3.57516	2.408772	1.382351
C33	-3.12908	2.075895	0.116685
H34	-6.94421	2.610838	0.849099
H35	-5.26558	2.850512	2.656667
H36	-2.85573	2.534058	2.18484
C37	-2.01878	-0.86677	1.146837
C38	-2.35716	-1.91587	2.059095
C39	-1.89692	-1.86591	3.399124
C40	-1.1131	-0.818	3.820582
C41	-0.76597	0.214451	2.922602
C42	-1.19985	0.218417	1.605625
H43	-2.17097	-2.66737	4.080123
H44	-0.75852	-0.77561	4.846206
H45	-0.1517	1.03782	3.276053
H46	-6.55157	1.432722	-3.82975
H47	-7.43972	2.097326	-1.58637
C48	-1.67361	1.962947	-0.21583
C49	-0.75649	1.286817	0.678187
C50	0.583861	1.617069	0.633232
C51	1.075187	2.600845	-0.24577
C52	0.232346	3.244353	-1.11151
C53	-1.14635	2.925764	-1.13938
H54	1.306981	1.081239	1.237516
F55	2.381494	2.889327	-0.23625
F56	0.695434	4.17908	-1.95462
H57	-1.80819	3.653639	-1.59685
C58	-0.94125	2.319936	-4.15082
H59	0.016041	1.865026	-3.9576
H60	-1.70587	1.78948	-4.69151
H61	-1.13022	3.329306	-3.82532
O62	-0.23273	3.039512	-5.86606
C63	0.289025	2.125807	-6.56114
O64	0.282184	0.887793	-6.39581
C65	1.104609	2.609088	-7.79208
F66	0.875788	3.898243	-8.08203
F67	2.420737	2.46366	-7.54154
F68	0.803575	1.876716	-8.87851
H69	-0.32376	-0.15445	-5.59617

Table S171. $[\text{Rh}^{\text{III-I}}(\text{bisq}^{\text{F2}})(\text{Me}_{\text{eq}}\cdots\text{TFAH})(\text{TFA})_2]^{\ddagger}$
(TFAH H-bonded to TFA_{ax}) thermodynamic values

Temp	298.15	498.15
E _{gas}	-2960.14	-2960.14
E _{solv}	-2960.17	-2960.17
G	-2959.78	-2959.87
ZPE	283.415	283.415
H _{vib}	26.528	66.623
S _{trans}	46.012	48.562
S _{rot}	38.946	40.476
S _{vib}	180.760	283.043
solv	-18.9	-18.9

Table S172. $[\text{Rh}^{\text{III-I}}(\text{bisq}^{\text{F2}})(\text{Me}_{\text{eq}}\cdots\text{TFAH})(\text{TFA})_2]^{\ddagger}$
(TFAH H-bonded to TFA_{eq}) Cartesian coordinates

Atom	x	y	z
Rh1	-1.61915	0.805003	-2.20789
N2	-2.04762	-0.86287	0.019413
C3	-2.65979	-1.99107	-0.28727
C4	-2.92047	-3.01981	0.649644
C5	-2.5082	-2.84846	1.948173
C6	-6.33886	1.536644	-1.62505
C7	-5.872	1.061447	-2.82851
C8	-4.48447	0.907793	-3.02678
N9	-3.59695	1.237492	-2.09401
H10	-2.95021	-2.10851	-1.3287
H11	-3.42771	-3.92429	0.329211
H12	-2.67899	-3.61622	2.69906
O13	-2.292	-0.83543	-3.30272
H14	-4.08474	0.462277	-3.92894
O15	0.492935	0.374513	-2.35594
C16	1.258188	-0.47439	-2.82605
O17	2.096468	-0.28992	-3.78143
C18	1.414892	-1.84176	-2.12375
F19	1.917212	-2.78175	-2.9211
F20	2.257507	-1.67442	-1.07778

F21	0.239314	-2.26573	-1.63513
C22	-1.64755	-1.63079	-4.08122
O23	-0.47025	-1.62069	-4.41965
C24	-2.59928	-2.72432	-4.6405
F25	-1.9737	-3.57417	-5.45752
F26	-3.14585	-3.4427	-3.62959
F27	-3.61886	-2.1554	-5.32544
C28	-4.02969	1.747262	-0.89035
C29	-5.41739	1.886558	-0.60608
C30	-5.80438	2.337968	0.681965
C31	-4.84762	2.636963	1.624997
C32	-3.47192	2.524092	1.318551
C33	-3.04871	2.089765	0.075463
H34	-6.86207	2.4336	0.910751
H35	-5.14429	2.974788	2.61343
H36	-2.73504	2.789702	2.06952
C37	-1.62744	-0.66906	1.303327
C38	-1.83486	-1.65588	2.318627
C39	-1.35882	-1.43008	3.635293
C40	-0.68412	-0.27044	3.936006
C41	-0.46616	0.703924	2.937109
C42	-0.92322	0.536218	1.638769
H43	-1.53006	-2.18895	4.394792
H44	-0.31451	-0.09611	4.942242
H45	0.067509	1.614864	3.193678
H46	-6.54882	0.778523	-3.62722
H47	-7.4044	1.638738	-1.43852
C48	-1.60422	2.057542	-0.31098
C49	-0.6035	1.542823	0.595859
C50	0.707591	1.960126	0.453245
C51	1.084818	2.869952	-0.54953
C52	0.158179	3.338768	-1.4447
C53	-1.19252	2.931234	-1.36534
H54	1.489094	1.553477	1.086522
F55	2.365543	3.252643	-0.63957
F56	0.520299	4.188215	-2.41718
H57	-1.92036	3.531655	-1.90036
C58	-0.96984	1.79289	-4.35926
H59	-0.7767	0.773148	-4.64632
H60	-1.90544	2.259252	-4.63121

H61	-0.22302	2.360413	-3.83768
O62	-0.15213	2.399251	-6.06761
C63	1.104223	2.255834	-6.09118
O64	1.874317	1.726029	-5.26658
C65	1.757155	2.890884	-7.35275
F66	1.565677	4.226508	-7.34959
F67	3.075977	2.661982	-7.40639
F68	1.20126	2.396304	-8.47533
H69	1.930746	0.585865	-4.31353

Table S173. $[\text{Rh}^{\text{III}}](\text{bisq}^{\text{F2}})(\text{Me}_{\text{eq}}\cdots\text{TFAH})(\text{TFA})_2]^{\dagger}$
(TFAH H-bonded to TFA_{eq}) thermodynamic values

Temp	298.15	498.15
E_{gas}	-2960.15	-2960.15
E_{solv}	-2960.18	-2960.18
G	-2959.78	-2959.87
ZPE	284.018	284.018
H_{vib}	26.363	66.431
S_{trans}	46.012	48.562
S_{rot}	38.932	40.462
S_{vib}	179.220	281.437
solv	-18.9	-18.9

Table S174. $[\text{Rh}^{\text{III}}](\text{bisq}^{\text{F2}})(\text{Me}_{\text{eq}}\cdots\text{TFA})(\text{TFA}_{\text{ax}})(\text{TFAH}_{\text{eq}})]^{\dagger}$ Cartesian coordinates

Atom	x	y	z
Rh1	-1.61598	0.704084	-2.14335
N2	-2.27696	-1.06061	-9.8E-05
C3	-2.95733	-2.12987	-0.36992
C4	-3.30332	-3.18537	0.506277
C5	-2.90726	-3.10469	1.818274
C6	-6.35027	1.573512	-1.84136
C7	-5.81291	1.155749	-3.03645
C8	-4.42269	0.944018	-3.13881
N9	-3.5989	1.163322	-2.11958
H10	-3.25226	-2.17617	-1.41445

H11	-3.86045	-4.03716	0.129882
H12	-3.1389	-3.89679	2.52596
O13	-2.24722	-0.83291	-3.45264
H14	-3.97293	0.551178	-4.04208
O15	0.500684	0.396062	-2.09975
C16	1.442596	-0.15129	-2.69043
O17	1.453993	-1.25845	-3.33263
C18	2.834356	0.493263	-2.5064
F19	3.725176	0.056447	-3.3874
F20	2.75293	1.825656	-2.56789
F21	3.267174	0.164386	-1.26081
H22	0.522122	-1.71124	-3.40647
C23	-1.80656	-1.96881	-3.80889
O24	-0.69216	-2.48757	-3.65798
C25	-2.90557	-2.82054	-4.502
F26	-2.40844	-3.89668	-5.11106
F27	-3.79979	-3.24201	-3.56962
F28	-3.58421	-2.0912	-5.40764
C29	-4.09885	1.623273	-0.92268
C30	-5.49706	1.812466	-0.73478
C31	-5.96212	2.212091	0.544343
C32	-5.06857	2.418131	1.570244
C33	-3.67883	2.266461	1.358482
C34	-3.18037	1.881076	0.127432
H35	-7.0288	2.347244	0.698295
H36	-5.42499	2.719315	2.550545
H37	-2.98979	2.47143	2.171364
C38	-1.88968	-0.94788	1.304652
C39	-2.17954	-1.97125	2.262924
C40	-1.73757	-1.8361	3.603305
C41	-1.02602	-0.72388	3.985136
C42	-0.73989	0.290961	3.04684
C43	-1.15451	0.210442	1.726108
H44	-1.96933	-2.62317	4.316201
H45	-0.68471	-0.61505	5.010212
H46	-0.18974	1.16934	3.372079
H47	-6.43598	0.965872	-3.90338
H48	-7.42099	1.7203	-1.73034
C49	-1.71264	1.855387	-0.16155
C50	-0.77255	1.27383	0.765481

C51	0.543419	1.705639	0.739341
C52	0.978868	2.69043	-0.15954
C53	0.113509	3.215845	-1.08819
C54	-1.23326	2.801035	-1.11906
H55	1.28622	1.257148	1.390201
F56	2.251962	3.092482	-0.12237
F57	0.532837	4.130714	-1.96635
H58	-1.92726	3.421151	-1.67566
C59	-1.08507	1.843893	-4.0462
H60	-1.15834	0.935956	-4.62097
H61	-1.86565	2.584734	-4.16612
H62	-0.1223	2.150522	-3.67846
O63	-0.23347	2.532243	-5.89787
C64	0.918419	1.997997	-5.9612
O65	1.505052	1.261307	-5.15586
C66	1.708545	2.38558	-7.24911
F67	2.458475	3.488711	-7.01413
F68	2.544435	1.403707	-7.63385
F69	0.901479	2.662439	-8.29216

Table S175. $[\text{Rh}^{\text{III}}]$
 $[(\text{bisq}^{\text{F2}})(\text{Me}_{\text{eq}}\cdots\text{TFA})(\text{TFA}_{\text{ax}})(\text{TFAH}_{\text{eq}})]^{\ddagger}$
thermodynamic values

Temp	298.15	498.15
E _{gas}	-2960.14	-2960.14
E _{solv}	-2960.18	-2960.18
G	-2959.79	-2959.87
ZPE	284.002	284.002
H _{vib}	27.013	67.462
S _{trans}	46.012	48.562
S _{rot}	38.961	40.491
S _{vib}	179.729	281.903
solv	-24.3	-24.3

Table S176. $[\text{Rh}^{\text{III}}]$
 $[(\text{bisq}^{\text{F2}})(\text{Me}_{\text{eq}}\cdots\text{TFA})(\text{TFA}_{\text{eq}})(\text{TFAH}_{\text{ax}})]^{\ddagger}$ Cartesian
coordinates

Atom	x	y	z
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Rh1	-1.12486	1.020471	-1.7747
N2	-1.98967	-0.99015	-0.06552
C3	-2.55132	-2.0197	-0.67258
C4	-3.00437	-3.17811	-3.5E-05
C5	-2.84387	-3.25035	1.36121
C6	-5.86706	1.879983	-2.07614
C7	-5.15835	1.650085	-3.23195
C8	-3.75887	1.473188	-3.17285
N9	-3.09579	1.538998	-2.02229
H10	-2.64492	-1.94285	-1.75261
H11	-3.45838	-3.9863	-0.56441
H12	-3.16707	-4.12467	1.920266
O13	-1.62823	-0.53347	-3.27471
H14	-3.17938	1.27111	-4.06945
O15	0.83711	0.473926	-1.32433
C16	1.753324	-0.06648	-2.00454
O17	1.751835	-0.509	-3.1687
C18	3.085518	-0.16404	-1.21348
F19	4.051201	-0.76052	-1.91653
F20	3.509676	1.069939	-0.8707
F21	2.898994	-0.8645	-0.07464
H22	0.689541	-0.78566	-4.04719
C23	-1.22694	-1.01032	-4.34529
O24	-0.02165	-1.1096	-4.76443
C25	-2.28069	-1.69524	-5.2421
F26	-1.8731	-1.84875	-6.49644
F27	-2.51815	-2.92238	-4.71236
F28	-3.4377	-1.02041	-5.22794
C29	-3.76728	1.819832	-0.85545
C30	-5.18102	1.971662	-0.83773
C31	-5.82319	2.188406	0.408446
C32	-5.07934	2.260311	1.564423
C33	-3.67033	2.145776	1.526756
C34	-3.00253	1.933209	0.334385
H35	-6.90436	2.291376	0.433776
H36	-5.57153	2.422299	2.518657
H37	-3.10419	2.237591	2.447518
C38	-1.82776	-1.03255	1.290537
C39	-2.2393	-2.1716	2.055072
C40	-2.03163	-2.20338	3.45739

C41	-1.42433	-1.14453	4.088451
C42	-1.01568	-0.01743	3.343563
C43	-1.20697	0.068986	1.973355
H44	-2.35704	-3.07639	4.017251
H45	-1.26035	-1.16456	5.161718
H46	-0.54816	0.816172	3.8602
H47	-5.64922	1.584282	-4.19658
H48	-6.9475	1.994381	-2.09593
C49	-1.50891	1.923125	0.237248
C50	-0.70184	1.245022	1.225984
C51	0.602366	1.65632	1.422014
C52	1.167391	2.709058	0.677164
C53	0.44448	3.324681	-0.30947
C54	-0.8926	2.935522	-0.57234
H55	1.250543	1.128888	2.113716
F56	2.430612	3.076896	0.921685
F57	0.984104	4.309644	-1.04245
H58	-1.50419	3.644613	-1.12032
C59	-0.46393	2.336681	-3.58089
H60	-0.11239	1.402253	-3.97862
H61	-1.47341	2.668305	-3.73977
H62	0.262769	3.04199	-3.20302
O63	-0.18307	2.955506	-5.52432
C64	-0.95296	2.245369	-6.24446
O65	-1.76167	1.362201	-5.91335
C66	-0.85072	2.532989	-7.77092
F67	-0.03693	3.559553	-8.06535
F68	-0.38893	1.442232	-8.41677
F69	-2.07095	2.820271	-8.27268

Table S177. [Rh^{III}]-
[(bisq^{F2})(Me_{eq}...TFA)(TFA_{eq})(TFAH_{ax})][†]
thermodynamic values

Temp	298.15	498.15
E_{gas}	-2960.15	-2960.15
E_{solv}	-2960.18	-2960.18
G	-2959.79	-2959.87
ZPE	283.912	283.912
H_{vib}	26.927	67.311

S_{trans}	46.012	48.562
S_{rot}	38.940	40.470
S_{vib}	179.500	281.504
solv	-19.7	-19.7

Table S178. [Rh^{III-II}](bisq^{F2})(Me_{ax}...OVCl₃)(TFA)₂][‡]
Cartesian coordinates

Atom	x	y	z
Rh1	-1.56603	0.114916	-2.10293
N2	-2.37761	-1.01055	-0.49998
C3	-3.24023	-2.00006	-0.70253
C4	-3.63579	-2.90354	0.301313
C5	-3.08569	-2.77673	1.552899
C6	-6.27731	1.326852	-2.30315
C7	-5.66017	0.870375	-3.44297
C8	-4.26024	0.688167	-3.44329
N9	-3.50205	0.969714	-2.38828
H10	-3.62666	-2.11645	-1.70726
H11	-4.32936	-3.69765	0.050137
H12	-3.32824	-3.47801	2.346728
H13	-3.73731	0.311458	-4.31654
O14	0.2106	-0.80301	-1.61002
C15	1.16654	-1.09481	-2.43682
O16	1.199858	-1.06658	-3.65409
C17	2.415562	-1.57426	-1.64413
F18	3.431794	-1.88133	-2.45331
F19	2.846199	-0.61137	-0.78801
F20	2.122951	-2.66517	-0.90373
O21	-0.61913	1.320542	-3.44532
C22	-0.9483	1.37963	-4.6895
O23	-1.82916	0.770803	-5.28624
C24	-0.05941	2.401144	-5.44647
F25	-0.44119	2.53157	-6.72287
F26	-0.14939	3.6199	-4.8606
F27	1.231421	2.030148	-5.42604
C28	-4.07653	1.560939	-1.28287
C29	-5.49215	1.697538	-1.18085
C30	-6.05058	2.213042	0.017724
C31	-5.23234	2.613934	1.048154

C32	-3.82683	2.567762	0.899866
C33	-3.23992	2.062746	-0.24494
H34	-7.13088	2.296246	0.099435
H35	-5.65957	3.009246	1.96471
H36	-3.19262	2.969883	1.684517
C37	-1.87817	-0.79859	0.767617
C38	-2.18858	-1.7142	1.822052
C39	-1.59818	-1.54434	3.100074
C40	-0.74682	-0.49206	3.332339
C41	-0.49003	0.443223	2.308098
C42	-1.04419	0.326504	1.043082
H43	-1.83102	-2.2607	3.882804
H44	-0.28354	-0.36037	4.305243
H45	0.147381	1.296867	2.518244
H46	-6.22164	0.606444	-4.33206
H47	-7.35851	1.426054	-2.25233
C48	-1.77284	2.230183	-0.50096
C49	-0.7562	1.408679	0.056515
C50	0.597659	1.749761	-0.17019
C51	0.923162	2.851509	-0.92786
C52	-0.08097	3.666497	-1.46898
C53	-1.40741	3.366315	-1.2522
H54	1.391567	1.109627	0.193345
F55	2.19879	3.160056	-1.17202
F56	0.268126	4.73179	-2.18998
H57	-2.16548	4.010536	-1.68351
C58	-1.72903	-1.77388	-3.57701
H59	-0.91427	-1.42479	-4.19528
H60	-1.5186	-2.47476	-2.78269
H61	-2.74291	-1.4703	-3.78862
O62	-2.00484	-3.35124	-4.84247
V63	-3.41424	-4.15587	-4.89583
Cl64	-3.75225	-4.988	-2.87771
Cl65	-5.00728	-2.66948	-5.23806
Cl66	-3.46836	-5.71933	-6.3914

Table S179. [Rh^{III-II}](bisq^{F2})(Me_{ax}...OVCl₃)(TFA)₂][‡]
thermodynamic values

Temp	298.15	498.15
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E_{gas}	-3960.72	-3960.72
E_{solv}	-3960.75	-3960.75
G	-3960.39	-3960.48
ZPE	264.268	264.268
H_{vib}	27.102	66.677
S_{trans}	46.214	48.764
S_{rot}	39.217	40.747
S_{vib}	185.911	286.983
solv	-21.3	-21.3

Table S180. [Rh^{III}-
^{II}(bisq^{F2})(Me_{ax}...OVCl₃)(TFA_{eq})(TFAH_{eq})]⁺⁺
Cartesian coordinates

Atom	x	y	z
Rh1	-1.22107	0.254294	-1.45548
N2	-1.71233	-1.12738	0.024625
C3	-1.85605	-2.42441	-0.22902
C4	-2.48985	-3.30857	0.663744
C5	-3.01475	-2.80785	1.833685
C6	-5.66809	2.290712	-1.39383
C7	-5.45639	0.991806	-1.7855
C8	-4.15859	0.468607	-1.68709
N9	-3.11131	1.149335	-1.22324
H10	-1.46616	-2.77893	-1.1764
H11	-2.58022	-4.35586	0.398322
H12	-3.55834	-3.45052	2.519834
H13	-3.97259	-0.54329	-2.01847
O14	0.524866	-0.94697	-1.66624
C15	1.75495	-0.83053	-1.83089
O16	2.413369	0.177325	-2.23604
C17	2.592603	-2.08151	-1.4732
F18	3.870526	-1.94197	-1.80431
F19	2.498979	-2.28788	-0.14628
F20	2.083121	-3.14957	-2.10584
O21	-0.99675	1.67996	-2.96873
C22	0.025608	2.293388	-3.39394
O23	1.234736	2.07647	-3.18629
C24	-0.32159	3.542191	-4.24527
F25	-0.74634	4.516186	-3.40242

F26	0.73201	3.996072	-4.91792
F27	-1.31167	3.276957	-5.10771
H28	1.808635	1.006062	-2.5977
C29	-3.30372	2.432147	-0.74317
C30	-4.59804	3.04181	-0.85556
C31	-4.79648	4.378842	-0.42593
C32	-3.75762	5.092584	0.116516
C33	-2.49766	4.480251	0.268256
C34	-2.24656	3.175646	-0.13353
H35	-5.78332	4.818902	-0.53345
H36	-3.9005	6.116281	0.446798
H37	-1.69512	5.040087	0.738741
C38	-2.09115	-0.62783	1.250572
C39	-2.82296	-1.44335	2.164782
C40	-3.29953	-0.86622	3.370219
C41	-3.02086	0.447722	3.665082
C42	-2.20518	1.214804	2.801171
C43	-1.72453	0.698954	1.61103
H44	-3.87087	-1.48236	4.057585
H45	-3.38231	0.88992	4.587877
H46	-1.91228	2.217462	3.09829
H47	-6.24972	0.372716	-2.18835
H48	-6.64733	2.752253	-1.48236
C49	-0.88533	2.630287	0.114698
C50	-0.65947	1.436267	0.849232
C51	0.672753	1.043177	1.121007
C52	1.73802	1.809268	0.693383
C53	1.509615	2.996583	-0.01216
C54	0.219021	3.396064	-0.30539
H55	0.876626	0.149731	1.701564
F56	2.992111	1.433024	0.947516
F57	2.551485	3.716249	-0.418
H58	0.076294	4.292928	-0.89787
C59	-1.90461	-1.11012	-3.43633
H60	-2.33838	-0.20209	-3.82969
H61	-0.85818	-1.31873	-3.60364
H62	-2.45758	-1.72986	-2.7506
O63	-2.47949	-2.22372	-4.85193
V64	-2.55005	-1.83257	-6.44335
Cl65	-3.71612	-0.01813	-6.55632

Cl66	-0.52229	-1.48709	-7.08078
Cl67	-3.48386	-3.41692	-7.53665

Table S181. [Rh^{III}-

^{II}(bisq^{F2})(Me_{ax}...OVCl₃)(TFA_{eq})(TFAH_{eq})]⁺
thermodynamic values

Temp	298.15	498.15
E_{gas}	-3961.10	-3961.10
E_{solv}	-3961.17	-3961.17
G	-3960.80	-3960.89
ZPE	271.490	271.490
H_{vib}	27.051	66.696
S_{trans}	46.217	48.767
S_{rot}	39.309	40.839
S_{vib}	185.779	286.995
solv	-40.1	-40.1

Table S182. [Rh^{III-II}(bisq^{F2})(Me_{eq}...OVCl₃)(TFA)₂]⁺
Cartesian coordinates

Atom	x	y	z
Rh1	-1.54538	0.82234	-2.14029
N2	-2.27455	-0.64542	-0.36733
C3	-3.01852	-1.64124	-0.81998
C4	-3.45706	-2.71886	-0.02234
C5	-3.08846	-2.75082	1.298149
C6	-6.26236	2.002562	-1.88163
C7	-5.77376	1.442694	-3.0388
C8	-4.39619	1.154686	-3.13841
N9	-3.54254	1.440275	-2.16336
H10	-3.29043	-1.59931	-1.86767
H11	-4.05633	-3.504	-0.47021
H12	-3.38554	-3.57061	1.946987
O13	-2.07121	-0.50652	-3.60839
H14	-3.9744	0.645759	-3.99939
O15	0.386237	0.256317	-1.86792
C16	1.198498	-0.11255	-2.80784
O17	1.05154	-0.10855	-4.01752
C18	2.54105	-0.57537	-2.17839

F19	3.419523	-0.96504	-3.10619
F20	3.101782	0.444097	-1.47668
F21	2.354682	-1.59656	-1.31872
C22	-1.63292	-1.72914	-3.71792
O23	-0.87328	-2.35839	-3.01049
C24	-2.36603	-2.4258	-4.89635
F25	-1.83705	-3.61714	-5.18203
F26	-3.66526	-2.62492	-4.52893
F27	-2.37501	-1.68241	-6.01499
C28	-3.99029	2.036546	-1.00757
C29	-5.37639	2.306029	-0.81592
C30	-5.80617	2.839754	0.425927
C31	-4.8919	3.089879	1.423192
C32	-3.5145	2.854035	1.210095
C33	-3.04655	2.346677	0.011254
H34	-6.86356	3.038681	0.575855
H35	-5.22058	3.490433	2.377296
H36	-2.80453	3.094819	1.995507
C37	-1.92079	-0.62844	0.958823
C38	-2.3069	-1.69648	1.832101
C39	-1.90956	-1.68513	3.193173
C40	-1.15277	-0.65013	3.686363
C41	-0.77974	0.411337	2.836546
C42	-1.14959	0.45055	1.501687
H43	-2.21367	-2.50946	3.832567
H44	-0.84388	-0.63897	4.727133
H45	-0.19337	1.232459	3.239316
H46	-6.42519	1.195387	-3.86976
H47	-7.32269	2.210096	-1.76575
C48	-1.57434	2.239878	-0.25164
C49	-0.68221	1.556433	0.638673
C50	0.673321	1.85467	0.611846
C51	1.187019	2.793448	-0.28512
C52	0.351693	3.41938	-1.19099
C53	-1.01835	3.14772	-1.18853
H54	1.375403	1.301121	1.225004
F55	2.492588	3.05824	-0.29621
F56	0.850303	4.278391	-2.09129
H57	-1.66327	3.765764	-1.80304
C58	-1.04036	2.147507	-4.17979

H59	-0.77723	1.205814	-4.6411
H60	-2.06494	2.48033	-4.13417
H61	-0.26172	2.738054	-3.72266
O62	-0.91081	3.265245	-5.82217
V63	0.075978	2.916787	-7.07745
Cl64	2.113301	3.025349	-6.33739
Cl65	-0.44186	0.927326	-7.7752
Cl66	-0.22414	4.352412	-8.67576

Table S183. $[\text{Rh}^{\text{III-II}}(\text{bisq}^{\text{F2}})(\text{Me}_{\text{eq}}\cdots\text{OVCl}_3)(\text{TFA})_2]^{\ddagger}$
thermodynamic values

Temp	298.15	498.15
E _{gas}	-3960.70	-3960.70
E _{solv}	-3960.73	-3960.73
G	-3960.38	-3960.47
ZPE	263.925	263.925
H _{vib}	26.747	65.953
S _{trans}	46.214	48.764
S _{rot}	39.239	40.769
S _{vib}	187.966	289.108
solv	-18.4	-18.4

Table S184. $[\text{Rh}^{\text{III-}}$
 $^{\text{II}}(\text{bisq}^{\text{F2}})(\text{Me}_{\text{eq}}\cdots\text{OVCl}_3)(\text{TFA}_{\text{ax}})(\text{TFAH}_{\text{eq}})]^{+\ddagger}$
Cartesian coordinates

Atom	x	y	z
Rh1	-1.27894	0.400056	-2.10909
N2	-1.98852	-0.98481	-0.26226
C3	-2.66466	-2.05676	-0.65825
C4	-3.13252	-3.0552	0.218906
C5	-2.86549	-2.9302	1.559542
C6	-5.95165	1.643875	-2.19829
C7	-5.404	1.01646	-3.29385
C8	-4.03223	0.69768	-3.29578
N9	-3.22916	1.01809	-2.28438
H10	-2.83516	-2.14835	-1.72525
H11	-3.67801	-3.90315	-0.18047
H12	-3.19139	-3.68445	2.270505

O13	-1.85107	-1.14576	-3.39664
H14	-3.59043	0.138832	-4.11054
O15	0.765109	-0.09724	-1.74201
C16	1.747508	-0.7341	-2.15233
O17	1.8625	-1.47443	-3.18619
C18	3.04608	-0.59534	-1.31862
F19	3.971389	-1.47361	-1.6831
F20	3.524634	0.649938	-1.48343
F21	2.758918	-0.77072	-0.0169
H22	0.992581	-1.57458	-3.77076
C23	-1.28625	-1.8308	-4.30776
O24	-0.09119	-1.88281	-4.63324
C25	-2.31127	-2.68384	-5.10088
F26	-1.73149	-3.42898	-6.03185
F27	-2.98297	-3.48359	-4.24914
F28	-3.20506	-1.86047	-5.6918
C29	-3.73414	1.693523	-1.19468
C30	-5.12395	1.993025	-1.10251
C31	-5.61032	2.6123	0.0778
C32	-4.74694	2.921554	1.104017
C33	-3.36298	2.662581	0.979226
C34	-2.84495	2.066418	-0.15675
H35	-6.67036	2.834057	0.156889
H36	-5.11971	3.390894	2.008774
H37	-2.69146	2.960276	1.778715
C38	-1.72844	-0.81507	1.079233
C39	-2.14726	-1.80336	2.029487
C40	-1.83419	-1.65294	3.405251
C41	-1.12141	-0.5625	3.841746
C42	-0.71371	0.418705	2.91496
C43	-1.00713	0.326454	1.562106
H44	-2.1644	-2.41871	4.10133
H45	-0.87488	-0.44621	4.892009
H46	-0.1659	1.285964	3.272493
H47	-6.00645	0.739351	-4.15135
H48	-7.01259	1.873968	-2.15974
C49	-1.36541	1.948855	-0.36216
C50	-0.50991	1.366875	0.636036
C51	0.825174	1.741029	0.685632
C52	1.359058	2.63441	-0.24962

C53	0.573473	3.131217	-1.27646
C54	-0.783	2.808799	-1.33522
H55	1.504439	1.290945	1.400942
F56	2.643116	2.967189	-0.18587
F57	1.110318	3.915758	-2.2175
H58	-1.40938	3.357463	-2.03061
C59	-0.50039	1.507346	-4.24249
H60	-0.19043	0.545451	-4.6205
H61	-1.52878	1.817773	-4.34677
H62	0.198795	2.122896	-3.70022
O63	0.053886	2.357134	-5.89641
V64	-0.79898	3.586922	-6.55679
Cl65	0.221257	4.4275	-8.23779
Cl66	-2.73202	2.759423	-7.09523
Cl67	-1.04928	5.045022	-4.96471

Table S185. [Rh^{III}-
^{II}(bisq^{F2})(Me_{eq}...OVCl₃)(TFA_{ax})(TFAH_{eq})]⁺⁺
thermodynamic values

Temp	298.15	498.15
E_{gas}	-3961.09	-3961.09
E_{solv}	-3961.15	-3961.15
G	-3960.78	-3960.87
ZPE	271.797	271.797
H_{vib}	27.102	66.792
S_{trans}	46.217	48.767
S_{rot}	39.283	40.813
S_{vib}	185.968	287.313
solv	-38.2	-38.2

Table S186. [Rh^{III}-
^{II}(bisq^{F2})(Me_{eq}...OVCl₃)(TFA_{eq})(TFAH_{ax})]⁺⁺
Cartesian coordinates

Atom	x	y	z
Rh1	-1.47157	0.630803	-2.05852
N2	-2.10942	-0.93146	-0.30788
C3	-2.83177	-1.9575	-0.73894
C4	-3.22139	-3.04271	0.069686

C5	-2.82977	-3.05127	1.385593
C6	-6.21477	1.527424	-1.83303
C7	-5.68061	1.032091	-3.00097
C8	-4.2903	0.825492	-3.09411
N9	-3.46368	1.122272	-2.095
H10	-3.12952	-1.93734	-1.78062
H11	-3.8028	-3.85001	-0.36156
H12	-3.0864	-3.87709	2.043374
O13	-1.903	-0.68112	-3.6348
H14	-3.84076	0.3793	-3.97339
O15	0.637039	0.330648	-1.94483
C16	1.397332	-0.63701	-1.7636
O17	1.164091	-1.88063	-1.91791
C18	2.818308	-0.34049	-1.22252
F19	3.714391	-1.17906	-1.73329
F20	3.176536	0.91696	-1.49922
F21	2.790964	-0.493	0.119712
H22	0.25944	-2.12231	-2.4333
C23	-1.60565	-1.90409	-3.81499
O24	-0.75085	-2.60472	-3.25037
C25	-2.55034	-2.61641	-4.81746
F26	-1.95689	-3.63831	-5.42351
F27	-3.60786	-3.08262	-4.1075
F28	-3.01937	-1.76519	-5.74159
C29	-3.95834	1.668341	-0.93073
C30	-5.35915	1.856116	-0.75232
C31	-5.8275	2.349315	0.492987
C32	-4.93679	2.645237	1.499431
C33	-3.54629	2.495267	1.293552
C34	-3.04533	2.022195	0.093953
H35	-6.89494	2.487026	0.636888
H36	-5.29456	3.020236	2.453018
H37	-2.85885	2.779473	2.08415
C38	-1.74989	-0.88444	1.01865
C39	-2.08379	-1.96363	1.901788
C40	-1.67389	-1.93101	3.259286
C41	-0.95831	-0.86257	3.742458
C42	-0.64274	0.211362	2.886164
C43	-1.02506	0.231677	1.552245
H44	-1.93843	-2.76334	3.905174

H45	-0.64317	-0.8319	4.780479
H46	-0.10186	1.063055	3.288333
H47	-6.30677	0.775386	-3.84783
H48	-7.28641	1.669238	-1.72586
C49	-1.57038	2.018037	-0.18261
C50	-0.63467	1.380454	0.705461
C51	0.68104	1.82724	0.739076
C52	1.115534	2.85321	-0.10384
C53	0.247745	3.429415	-1.01987
C54	-1.08572	3.033247	-1.05612
H55	1.418785	1.340345	1.366584
F56	2.381972	3.248221	-0.06382
F57	0.691245	4.364754	-1.86574
H58	-1.77605	3.612128	-1.66044
C59	-0.85599	2.024481	-4.06844
H60	-0.87698	1.121272	-4.65791
H61	-1.77247	2.569531	-3.89389
H62	0.056949	2.308337	-3.56741
O63	-0.4477	3.10827	-5.60876
V64	-0.55882	4.734135	-5.73941
Cl65	-1.04526	5.255342	-7.7579
Cl66	-2.19051	5.284329	-4.40633
Cl67	1.295906	5.576591	-5.05092

Table S187. $[\text{Rh}^{\text{III}}\text{-(bisq}^{\text{F2}}\text{)(Me}_{\text{eq}}\cdots\text{OVCl}_3\text{)(TFA}_{\text{eq}}\text{)(TFAH}_{\text{ax}}\text{)}]]^{+\ddagger}$
thermodynamic values

Temp	298.15	498.15
E _{gas}	-3961.10	-3961.10
E _{solv}	-3961.16	-3961.16
G	-3960.79	-3960.87
ZPE	271.626	271.626
H _{vib}	27.590	67.657
S _{trans}	46.217	48.767
S _{rot}	39.312	40.842
S _{vib}	184.957	286.241
solv	-38.2	-38.2

Table S188.

$[\text{Rh}^{\text{III}}\text{-(bisq}^{\text{F2}}\text{)(CH}_2\text{TFA}_{\text{ax}}\cdots\text{H}\cdots\text{TFA}_{\text{eq}}\text{)(TFA}_{\text{eq}}\text{)}]]^{+\ddagger}$
Cartesian coordinates

Atom	x	y	z
Rh1	-2.7722	0.324143	-1.54148
N2	-1.61416	-0.72976	-0.08065
C3	-1.89318	-2.01428	0.125234
C4	-1.10826	-2.86476	0.920487
C5	0.020929	-2.35476	1.511387
C11	-6.3094	-0.46023	1.723853
C12	-6.5159	-0.90339	0.438027
C13	-5.5565	-0.61639	-0.55337
N14	-4.46648	0.100655	-0.30785
H15	-2.76986	-2.40052	-0.37319
H16	-1.39969	-3.90327	1.023402
H17	0.677668	-2.98278	2.106375
H23	-5.67912	-1.00833	-1.55278
O28	-1.02485	0.715789	-2.59985
C29	-0.46253	-0.27565	-3.14625
O30	-0.89382	-1.45184	-3.14834
C31	0.912223	0.001018	-3.79823
F32	1.103388	-0.78147	-4.85539
F33	1.018472	1.281104	-4.16618
F34	1.864743	-0.25953	-2.8793
O35	-3.86954	1.43925	-2.85895
C36	-3.61832	1.37245	-4.1397
O37	-2.92783	0.567225	-4.73726
C38	-4.34034	2.521298	-4.89489
F39	-4.20749	2.390983	-6.21248
F40	-5.65096	2.545877	-4.59164
F41	-3.80225	3.703963	-4.52319
H42	-2.18269	-1.33011	-2.81105
C43	-3.50767	-1.52362	-2.92075
H44	-3.21931	-1.91602	-3.9033
H46	-4.34268	-0.85459	-3.09247
C41	0.336458	-0.98408	1.350895
C42	-0.53153	-0.16184	0.563018
C35	-0.24462	1.234186	0.451431
C44	0.904231	1.73014	1.055291

C45	1.779985	0.910481	1.793409
C46	1.493266	-0.42329	1.95044
H50	1.116474	2.792226	0.982821
H51	2.665351	1.343731	2.246609
H52	2.144531	-1.07023	2.530324
C47	-4.29709	0.659346	0.941244
C48	-5.17977	0.345427	2.013018
C49	-4.89676	0.867615	3.301874
C50	-3.80916	1.688468	3.494165
C51	-2.9966	2.06887	2.400803
C52	-3.23368	1.576623	1.130783
H55	-5.55608	0.617527	4.127054
H56	-3.59375	2.087888	4.479907
H57	-2.19934	2.789345	2.55605
H53	-7.00807	-0.70646	2.518239
H54	-7.38275	-1.49729	0.172031
C55	-1.13381	2.184309	-0.2528
C56	-2.56201	2.161033	-0.08401
C57	-3.34057	3.175125	-0.73823
C58	-2.75069	4.118296	-1.53476
C59	-1.35241	4.103705	-1.70561
C60	-0.55987	3.154985	-1.08327
H63	-4.41398	3.209871	-0.59336
F59	-3.46013	5.064625	-2.13739
F60	-0.80431	5.01083	-2.49507
H66	0.502334	3.15331	-1.29701
O62	-3.94356	-2.59931	-2.07326
C63	-3.84822	-3.86601	-2.54217
O64	-3.4384	-4.20914	-3.61351
C65	-4.36499	-4.82989	-1.45033
F66	-3.59684	-4.70924	-0.33703
F67	-5.62639	-4.51738	-1.1111
F68	-4.316	-6.08444	-1.86813

Table S189.

$[\text{Rh}^{\text{III}}(\text{bisq}^{\text{F2}})(\text{CH}_2\text{TFA}_{\text{ax}}\cdots\text{H}\cdots\text{TFA}_{\text{eq}})(\text{TFA}_{\text{eq}})]^{+\ddagger}$
thermodynamic values

Temp	298.15	498.15
E_{gas}	-2959.29	-2959.29

E_{solv}	-2959.37	-2959.37
G	-2958.98	-2959.06
ZPE	277.240	277.240
H_{vib}	25.327	64.760
S_{trans}	46.008	48.558
S_{rot}	38.687	40.217
S_{vib}	170.295	270.874
solv	-47.8	-47.8

Table S190.

$[\text{Rh}^{\text{III}}(\text{bisq}^{\text{F2}})(\text{CH}_2\text{TFA}_{\text{eq}}\cdots\text{H}\cdots\text{TFA}_{\text{ax}})(\text{TFA}_{\text{eq}})]^{+\ddagger}$
Cartesian coordinates

Atom	x	y	z
Rh1	-1.40422	0.20663	-1.61292
N2	-1.9244	-1.21088	-0.14583
C3	-2.13209	-2.48979	-0.43399
C4	-2.62908	-3.39878	0.521523
C5	-2.93807	-2.94957	1.785017
C11	-6.12248	1.636275	-1.43461
C12	-5.70092	0.512392	-2.10059
C13	-4.33017	0.210652	-2.11524
N14	-3.40525	0.949842	-1.50266
H15	-1.92633	-2.79983	-1.45066
H16	-2.77725	-4.43333	0.233507
H17	-3.35349	-3.62256	2.529147
H22	-3.96956	-0.65766	-2.65102
O27	0.410143	-0.74206	-1.60936
C28	1.508353	-0.16207	-1.99706
O29	1.653375	0.954544	-2.46651
C30	2.736016	-1.06456	-1.70249
F31	2.921064	-1.10814	-0.36126
F32	2.540578	-2.31989	-2.1374
F33	3.839916	-0.58019	-2.26559
H34	-0.01223	1.963164	-3.88577
H35	-0.57791	0.511468	-3.66071
O36	-1.96618	-1.22302	-3.00165
C37	-1.28554	-1.31114	-4.07329
O38	-0.43695	-0.48542	-4.46114
C39	-1.60337	-2.55398	-4.93607

F40	-0.77609	-2.65259	-5.96682
F41	-1.50037	-3.65443	-4.17216
F42	-2.86583	-2.45567	-5.38082
C43	-0.92521	1.769406	-3.30673
H45	-0.89747	2.512394	-2.52015
C41	-5.17593	2.45643	-0.77721
C42	-3.79352	2.080429	-0.80608
C35	-2.84337	2.920375	-0.15189
C44	-3.28135	4.088879	0.45373
C45	-4.64037	4.459588	0.476156
C46	-5.57384	3.650407	-0.12214
H50	-2.5521	4.728553	0.941722
H51	-4.93759	5.380401	0.967032
H52	-6.62664	3.916158	-0.11999
C47	-2.13706	-0.74936	1.127739
C48	-2.69805	-1.5958	2.128093
C49	-2.96614	-1.04919	3.409473
C50	-2.65976	0.266189	3.676943
C51	-2.03856	1.072532	2.695092
C52	-1.76735	0.580256	1.430754
H55	-3.40375	-1.68492	4.173196
H56	-2.86127	0.685404	4.657434
H57	-1.74192	2.085839	2.950207
H53	-7.17157	1.916798	-1.41245
H54	-6.39037	-0.13581	-2.62901
C55	-1.39495	2.607399	-0.08855
C56	-0.9228	1.3758	0.466232
C57	0.490437	1.191832	0.614725
C58	1.371369	2.166459	0.223829
C59	0.885403	3.374891	-0.31255
C60	-0.47199	3.593032	-0.47581
H63	0.879225	0.280562	1.055059
F59	2.682846	2.003734	0.351311
F60	1.757681	4.297486	-0.67989
H66	-0.80565	4.515716	-0.93783
O62	-2.06364	1.977356	-4.1717
C63	-2.76225	3.104684	-4.01547
O64	-2.56622	3.974565	-3.20268
C65	-3.93144	3.128377	-5.02558
F66	-3.49198	2.947329	-6.27485

F67	-4.79242	2.127861	-4.72626
F68	-4.58389	4.285432	-4.94912

Table S191.

$[\text{Rh}^{\text{III}}(\text{bisq}^{\text{F2}})(\text{CH}_2\text{TFA}_{\text{eq}}\cdots\text{H}\cdots\text{TFA}_{\text{ax}})(\text{TFA}_{\text{eq}})]^{+\ddagger}$
thermodynamic values

Temp	298.15	498.15
E _{gas}	-2959.30	-2959.30
E _{solv}	-2959.37	-2959.37
G	-2958.98	-2959.07
ZPE	277.512	277.512
H _{vib}	25.276	64.631
S _{trans}	46.008	48.558
S _{rot}	38.635	40.165
S _{vib}	169.638	270.012
solv	-45.1	-45.1

Table S192.

$[\text{Rh}^{\text{III}}(\text{bisq}^{\text{F2}})(\text{CH}_2\text{TFA}_{\text{eq}}\cdots\text{H}\cdots\text{TFA}_{\text{eq}})(\text{TFA}_{\text{ax}})]^{+\ddagger}$
Cartesian coordinates

Atom	x	y	z
Rh1	-2.48444	0.064502	-1.48307
N2	-1.32058	-1.23878	-0.30918
C3	-1.33437	-2.55324	-0.49623
C4	-0.7145	-3.4425	0.404547
C5	-0.11011	-2.94594	1.536244
C11	-5.67946	0.163516	2.221953
C12	-5.59062	-0.90417	1.36313
C13	-4.65975	-0.85551	0.31228
N14	-3.84267	0.177158	0.115045
H15	-1.88057	-2.91608	-1.35749
H16	-0.75088	-4.50602	0.197564
H17	0.341827	-3.61217	2.265566
H23	-4.5858	-1.66447	-0.40458
O28	-1.07063	-0.25149	-2.97254
C29	-1.09752	0.563646	-3.94002
O30	-1.89107	1.527427	-4.058
C31	0.008808	0.372943	-5.00203

F32	1.166312	0.822442	-4.47613
F33	0.147489	-0.92099	-5.30221
F34	-0.25973	1.059233	-6.10799
H35	-4.31858	1.226573	-3.825
H36	-2.85535	1.325262	-3.18132
O37	-3.43089	-1.6011	-2.14197
C38	-3.67936	-1.83705	-3.41074
O39	-3.52109	-1.11224	-4.36774
C40	-4.25003	-3.27651	-3.54913
F41	-4.57357	-3.54952	-4.8058
F42	-3.32252	-4.1688	-3.13237
F43	-5.34062	-3.42078	-2.77115
C44	-4.14734	1.2048	-2.74166
H45	-4.80091	0.423202	-2.3657
C41	-3.89274	1.266219	0.961502
C42	-4.83527	1.284575	2.038131
C43	-4.9245	2.425255	2.875404
C36	-4.12579	3.519207	2.646586
C45	-3.19963	3.500122	1.584016
C46	-3.05443	2.398642	0.752385
H49	-5.64826	2.422008	3.684796
H50	-4.20117	4.400278	3.275273
H51	-2.56744	4.367362	1.418294
C48	-0.65173	-0.70194	0.763156
C49	-0.06414	-1.54576	1.750788
C50	0.550444	-0.9467	2.879931
C51	0.597104	0.423861	2.998537
C52	0.074431	1.247564	1.975623
C53	-0.53918	0.704012	0.861037
H55	0.990714	-1.58555	3.639714
H56	1.068652	0.882461	3.861645
H57	0.184992	2.325414	2.051588
H53	-6.22947	-1.77432	1.460914
H54	-6.39793	0.170195	3.036499
C55	-0.89106	1.578116	-0.31177
C56	-2.01252	2.459922	-0.31197
C57	-2.01887	3.56919	-1.18931
C58	-0.95284	3.797298	-2.02876
C59	0.155584	2.924514	-2.04622
C60	0.188798	1.839431	-1.20942

H63	-2.86434	4.243903	-1.22075
F59	-0.94785	4.837485	-2.84993
F60	1.157844	3.185758	-2.8796
H66	1.064849	1.200734	-1.21045
O62	-4.56862	2.480523	-2.21854
C63	-5.71741	2.49917	-1.5301
O64	-6.40862	1.553869	-1.24514
C65	-6.10694	3.934883	-1.10589
F66	-5.11805	4.826022	-1.30929
F67	-7.17957	4.326665	-1.7965
F68	-6.40582	3.935477	0.202388

Table S193.

$[\text{Rh}^{\text{III}}(\text{bisq}^{\text{F2}})(\text{CH}_2\text{TFA}_{\text{eq}}\cdots\text{H}\cdots\text{TFA}_{\text{eq}})(\text{TFA}_{\text{ax}})]^{++}$
thermodynamic values

Temp	298.15	498.15
E_{gas}	-2959.30	-2959.30
E_{solv}	-2959.37	-2959.37
G	-2958.99	-2959.07
ZPE	277.579	277.579
H_{vib}	25.153	64.512
S_{trans}	46.008	48.558
S_{rot}	38.621	40.151
S_{vib}	168.923	269.316
solv	-44.5	-44.5

Rh(bisq^{F4}) complexes

Table S194. Rh^I(bisq^{F4})(TFA)(TFAH) Cartesian coordinates

Atom	x	y	z
Rh1	-1.21929	0.679835	-1.69717
N2	-2.17828	-0.3561	-0.14279
C3	-3.02741	-1.26853	-0.61591
C4	-3.66142	-2.24045	0.178392
C5	-3.39257	-2.26625	1.523962
C6	-5.47305	2.845876	-2.03279
C7	-4.81812	2.365539	-3.14238

C8	-3.48855	1.920804	-3.01227
N9	-2.81664	1.966853	-1.86093
H10	-3.19719	-1.23548	-1.6859
H11	-4.33373	-2.95252	-0.28757
H12	-3.84407	-3.00807	2.176954
H13	-2.94813	1.497052	-3.85062
O14	0.274236	-0.83792	-1.44956
C15	1.50166	-0.78443	-1.30493
O16	2.318798	0.149843	-1.61973
C17	2.156049	-2.00848	-0.62555
F18	3.487823	-1.91626	-0.56942
F19	1.685028	-2.12383	0.63182
F20	1.834844	-3.13045	-1.29451
O21	-0.53126	1.550913	-3.47203
C22	0.58779	2.063428	-3.7169
O23	1.663539	1.98552	-3.07418
C24	0.667162	2.884967	-5.02734
F25	1.350602	4.025286	-4.84018
F26	1.30299	2.166889	-5.97639
F27	-0.55052	3.20358	-5.49946
H28	1.907444	0.970421	-2.2106
C29	-3.39403	2.586955	-0.77164
C30	-4.76922	2.977759	-0.80942
C31	-5.37858	3.505476	0.358377
C32	-4.64395	3.685154	1.504882
C33	-3.26079	3.398348	1.507049
C34	-2.6233	2.871099	0.398255
H35	-6.43034	3.776099	0.321046
H36	-5.10877	4.088842	2.399206
H37	-2.66996	3.62956	2.388261
C39	-1.91318	-0.3324	1.211121
C40	-2.50876	-1.30982	2.077309
C41	-2.208	-1.31717	3.462644
C42	-1.34876	-0.38622	3.989026
C43	-0.77981	0.589635	3.146715
C44	-1.04355	0.647535	1.786975
H45	-2.6681	-2.07461	4.091123
H46	-1.10787	-0.38841	5.047588
H47	-0.11361	1.331801	3.575355
H49	-5.3102	2.288458	-4.10601

H50	-6.51561	3.148176	-2.08026
C51	-1.12887	2.783564	0.396151
C52	-0.3952	1.751433	1.023254
C53	0.998721	1.82753	1.014473
C54	1.681367	2.885342	0.420568
C55	0.959042	3.908479	-0.17677
C56	-0.43172	3.846601	-0.17733
F55	1.735526	0.839485	1.557053
F56	3.015372	2.913508	0.421766
F57	1.590055	4.937839	-0.74527
F58	-1.102	4.84993	-0.77095

Table S195. Rh^I(bisq^{F4})(TFA)(TFAH)
thermodynamic values

Temp	298.15	498.15
E_{gas}	-2592.62	-2592.62
E_{solv}	-2592.64	-2592.64
G	-2592.32	-2592.40
ZPE	231.541	231.541
H_{vib}	22.462	56.695
S_{trans}	45.660	48.210
S_{rot}	37.998	39.528
S_{vib}	147.767	234.221
solv	-15.0	-15.0

Table S196. Rh^I(bisq^{F4})(κ¹-TFA) Cartesian
coordinates

Atom	x	y	z
Rh1	-0.78669	0.670161	-1.96123
N2	-2.49296	-0.66773	0.499011
C3	-3.47593	-1.5113	0.260384
C4	-4.27157	-2.10525	1.269554
C5	-4.0019	-1.79239	2.579456
C6	-5.13867	2.650777	-2.51942
C7	-4.58577	1.919273	-3.54694
C8	-3.29462	1.372459	-3.39639
N9	-2.58203	1.541943	-2.28833
H10	-3.66077	-1.7491	-0.78672

H11	-5.06799	-2.79228	1.001094
H12	-4.57998	-2.22603	3.391971
H13	-2.82845	0.780084	-4.17736
O14	0.961413	-0.59643	-1.95376
C15	0.505717	-1.21579	-2.95845
O16	-0.59768	-0.91355	-3.49678
C17	1.340783	-2.34965	-3.57808
F18	2.054221	-1.87081	-4.61757
F19	2.195104	-2.87306	-2.68852
F20	0.547808	-3.33253	-4.03573
C21	-4.40007	2.850548	-1.32518
C22	-3.10001	2.281409	-1.25149
C23	-2.2852	2.431724	-0.10173
C24	-2.79156	3.142105	0.969731
C25	-4.09184	3.700374	0.921473
C26	-4.8815	3.567114	-0.19864
H27	-2.18783	3.27532	1.860966
H28	-4.46299	4.247869	1.782921
H29	-5.87685	4.001292	-0.23373
C30	-2.94754	-0.89384	2.885444
C31	-2.20888	-0.33887	1.790197
C32	-1.13183	0.570528	2.063788
C33	-0.83749	0.867069	3.386508
C34	-1.56975	0.316311	4.460161
C35	-2.61146	-0.54728	4.218172
H36	-0.02096	1.548053	3.603641
H37	-1.30335	0.584174	5.478407
H38	-3.1848	-0.97585	5.036433
H39	-5.12378	1.750303	-4.47347
H40	-6.1346	3.076012	-2.60992
C41	-0.90502	1.856902	-0.16803
C42	-0.31549	1.175936	0.97885
C43	1.055194	1.109163	1.043453
C44	1.918471	1.729529	0.094731
C45	1.399102	2.422916	-0.9549
C46	-0.02281	2.453663	-1.16162
F47	1.679758	0.425094	2.017855
F48	3.239124	1.611526	0.264404
F49	2.186161	3.068828	-1.81903
F50	-0.45187	3.553588	-1.85207

Table S197. Rh^I(bisq^{F4})(κ¹-TFA) thermodynamic values

Temp	298.15	498.15
E _{gas}	-2065.83	-2065.83
E _{solv}	-2065.85	-2065.85
G	-2065.56	-2065.62
ZPE	207.022	207.022
H _{vib}	17.621	46.018
S _{trans}	45.157	47.707
S _{rot}	37.274	38.804
S _{vib}	112.918	184.569
solv	-12.6	-12.6

Table S198. Rh^I(bisq^{F4})(κ²-TFA) Cartesian coordinates

Atom	x	y	z
Rh1	-1.42512	0.486345	-2.06553
N2	-2.20497	-0.70804	-0.5636
C3	-2.96673	-1.72705	-0.96202
C4	-3.69531	-2.54887	-0.08166
C5	-3.63114	-2.29647	1.266419
C6	-5.52898	3.071088	-1.61529
C7	-5.35007	2.108305	-2.57762
C8	-4.10457	1.45915	-2.66535
N9	-3.07182	1.726996	-1.86546
H10	-3.00133	-1.89164	-2.03257
H11	-4.29686	-3.35632	-0.48499
H12	-4.18885	-2.89585	1.980758
H13	-3.93103	0.688636	-3.40724
O14	-0.27682	1.336491	-3.70116
C15	0.569508	0.413057	-3.53068
O16	0.382494	-0.52819	-2.70768
C17	1.911592	0.490459	-4.27467
F18	2.797874	1.189051	-3.527
F19	2.426501	-0.72911	-4.49251
F20	1.786671	1.114722	-5.45546
C21	-4.45241	3.410718	-0.76023

C22	-3.20209	2.726835	-0.91953
C23	-2.09624	3.116476	-0.09991
C24	-2.28232	4.113791	0.842522
C25	-3.52359	4.759085	1.023261
C26	-4.58951	4.417299	0.229046
H27	-1.43467	4.413411	1.451516
H28	-3.62208	5.532548	1.778883
H29	-5.54937	4.915322	0.335333
C30	-2.81108	-1.24348	1.740544
C31	-2.07667	-0.45983	0.790451
C32	-1.1983	0.56059	1.273368
C33	-1.11593	0.779203	2.638282
C34	-1.86813	0.032667	3.569765
C35	-2.69697	-0.96794	3.126877
H36	-0.4359	1.545403	2.998343
H37	-1.77311	0.243758	4.630398
H38	-3.26982	-1.57128	3.825939
H39	-6.14264	1.830739	-3.26405
H40	-6.47796	3.587908	-1.50193
C41	-0.71574	2.559067	-0.24921
C42	-0.2974	1.365421	0.389247
C43	1.045174	0.998417	0.307244
C44	1.970015	1.747449	-0.4171
C45	1.559834	2.917044	-1.04257
C46	0.230532	3.320294	-0.93414
F47	1.476393	-0.1255	0.905581
F48	3.242852	1.350965	-0.50101
F49	2.435558	3.653047	-1.7322
F50	-0.1338	4.461293	-1.54579

Table S199. Rh^I(bisq^{F4})(κ²-TFA) thermodynamic values

Temp	298.15	498.15
E_{gas}	-2065.82	-2065.82
E_{solv}	-2065.85	-2065.85
G	-2065.56	-2065.62
ZPE	207.087	207.087
H_{vib}	17.747	46.174
S_{trans}	45.157	47.707

S_{rot}	37.070	38.600
S_{vib}	114.011	185.745
solv	-16.2	-16.2

Table S200. Rh^I(bisq^{F4})(Me) Cartesian coordinates

Atom	x	y	z
Rh1	-1.08031	0.834294	-1.82412
N2	-2.30323	-0.29789	-0.35454
C3	-3.35506	-1.04279	-0.66435
C4	-4.06592	-1.8109	0.281458
C5	-3.65532	-1.7935	1.594077
C6	-5.51962	2.991645	-2.04126
C7	-5.15266	2.340197	-3.19424
C8	-3.83843	1.830389	-3.30166
N9	-2.92469	1.965239	-2.35224
H10	-3.65634	-1.032	-1.70854
H11	-4.91928	-2.39971	-0.03882
H12	-4.174	-2.37529	2.35169
H13	-3.52704	1.290359	-4.19144
C22	-4.57077	3.166159	-1.00026
C23	-3.25167	2.663427	-1.20577
C24	-2.25495	2.846551	-0.19594
C25	-2.61456	3.464455	0.986333
C26	-3.93413	3.92438	1.210133
C27	-4.89045	3.796136	0.231155
H28	-1.8612	3.612501	1.754415
H29	-4.18071	4.398654	2.155716
H30	-5.9007	4.166191	0.385582
C31	-2.53501	-1.00954	1.969004
C32	-1.87845	-0.25526	0.948978
C33	-0.74476	0.552312	1.257925
C34	-0.29241	0.556291	2.569567
C35	-0.9294	-0.19692	3.580519
C36	-2.03583	-0.96276	3.294974
H37	0.573849	1.155776	2.828693
H38	-0.53787	-0.16151	4.593126
H39	-2.53143	-1.5437	4.068172
H40	-5.85055	2.197652	-4.01298

H41	-6.52848	3.374099	-1.90953
C42	-0.82169	2.451902	-0.49162
C43	-0.08339	1.38347	0.204473
C44	1.340821	1.48255	0.245522
C45	2.037485	2.534469	-0.28964
C46	1.331292	3.597137	-0.89845
C47	-0.03115	3.553823	-0.98233
F40	2.044915	0.495121	0.84195
F41	3.381018	2.569659	-0.2659
F42	2.025148	4.624255	-1.41124
F43	-0.67428	4.573389	-1.5911
C52	0.110083	1.584431	-3.30944
H53	1.156772	1.671924	-2.99116
H54	0.042653	0.834618	-4.11727
H55	-0.21529	2.551393	-3.71065

Table S201. Rh^I(bisq^{F4})(Me) thermodynamic values

Temp	298.15	498.15
E_{gas}	-1579.50	-1579.50
E_{solv}	-1579.51	-1579.51
G	-1579.21	-1579.27
ZPE	210.849	210.849
H_{vib}	14.759	39.750
S_{trans}	44.644	47.194
S_{rot}	36.090	37.620
S_{vib}	92.583	155.577
solv	-11.9	-11.9

Table S202. Rh^I(bisq^{F4})(Me)(TFAH) Cartesian coordinates

Atom	x	y	z
Rh1	-1.3972	0.582468	-2.28789
N2	-2.29138	-0.4711	-0.45338
C3	-3.25807	-1.29656	-0.83602
C4	-3.99585	-2.11305	0.044166
C5	-3.68795	-2.07728	1.381203
C6	-5.46458	3.128955	-1.93073

C7	-5.18664	2.417277	-3.07242
C8	-3.93205	1.789609	-3.20455
N9	-2.98012	1.854039	-2.27251
H10	-3.45525	-1.31937	-1.90343
H11	-4.77587	-2.75734	-0.34758
H12	-4.21738	-2.69788	2.099639
H13	-3.69338	1.198368	-4.07994
O14	0.15302	-0.89702	-2.11917
C15	1.31155	-0.77	-2.49673
O16	1.766498	0.159481	-3.3054
C17	2.41489	-1.71553	-1.99871
F18	3.15565	-2.16701	-3.02348
F19	3.221686	-1.05265	-1.15109
F20	1.885366	-2.76058	-1.35809
H21	1.000429	0.74221	-3.54246
C22	-4.46977	3.249237	-0.92686
C23	-3.20385	2.623391	-1.14633
C24	-2.16851	2.775686	-0.18063
C25	-2.43933	3.477498	0.982373
C26	-3.70289	4.057881	1.22397
C27	-4.69623	3.960512	0.278783
H28	-1.64743	3.599902	1.714878
H29	-3.87536	4.599236	2.14953
H30	-5.66674	4.422852	0.438563
C31	-2.65354	-1.22564	1.839152
C32	-1.96724	-0.40605	0.881197
C33	-0.91923	0.458442	1.346493
C34	-0.59484	0.442582	2.695228
C35	-1.26859	-0.37136	3.627725
C36	-2.28936	-1.1882	3.208759
H37	0.205625	1.088303	3.041941
H38	-0.97762	-0.34143	4.673533
H39	-2.82742	-1.81999	3.910531
H40	-5.91635	2.311936	-3.86852
H41	-6.4299	3.604418	-1.78216
C42	-0.76206	2.297039	-0.41352
C43	-0.14228	1.344472	0.445145
C44	1.250504	1.216094	0.406551
C45	2.050581	2.018757	-0.39854
C46	1.449633	3.003005	-1.18328

C47	0.073483	3.145226	-1.16536
F48	1.871772	0.275822	1.147271
F49	3.38152	1.864278	-0.41363
F50	2.206116	3.793543	-1.95653
F51	-0.47533	4.109169	-1.92786
C52	-0.79323	1.356602	-4.13847
H53	0.05093	2.074812	-4.12637
H54	-0.56342	0.574761	-4.87985
H55	-1.61445	1.947389	-4.56383

Table S203. Rh^I(bisq^{F4})(Me)(TFAH)
thermodynamic values

Temp	298.15	498.15
E_{gas}	-2106.28	-2106.28
E_{solv}	-2106.30	-2106.30
G	-2105.97	-2106.03
ZPE	236.728	236.728
H_{vib}	19.522	50.454
S_{trans}	45.233	47.783
S_{rot}	37.173	38.703
S_{vib}	126.826	204.897
solv	-11.3	-11.3

Table S204. Rh^{II}(bisq^{F4})(TFA)₂ Cartesian
coordinates

Atom	x	y	z
Rh1	-0.91338	0.775323	-1.97024
N2	-1.857	-0.52194	-0.59999
C3	-2.57886	-1.51221	-1.11503
C4	-3.30593	-2.42401	-0.32535
C5	-3.26204	-2.29925	1.041366
C6	-5.33415	2.842977	-2.07436
C7	-4.88167	2.073546	-3.11828
C8	-3.55702	1.590092	-3.09139
N9	-2.71579	1.860689	-2.09863
H10	-2.55095	-1.60388	-2.19504
H11	-3.87618	-3.20807	-0.81099
H12	-3.80568	-2.98434	1.686323

H13	-3.14858	0.988244	-3.89735
O14	0.822532	-0.36294	-1.86768
C15	0.631734	-1.38346	-2.62254
O16	-0.40108	-1.65548	-3.24062
C17	1.846673	-2.33814	-2.68691
F18	1.66879	-3.30241	-3.60021
F19	2.97656	-1.67536	-2.99078
F20	2.026534	-2.93473	-1.48581
O21	0.066541	1.998273	-3.31089
C22	-0.31826	1.875188	-4.5339
O23	-1.23848	1.195691	-4.98046
C24	0.533063	2.740896	-5.49761
F25	0.175502	2.552577	-6.77571
F26	0.374593	4.053668	-5.21445
F27	1.843789	2.451788	-5.38497
C29	-4.45429	3.17636	-1.01414
C30	-3.11418	2.683703	-1.07068
C31	-2.18538	3.060969	-0.05762
C32	-2.62196	3.855804	0.986291
C33	-3.95803	4.306106	1.069994
C34	-4.85567	3.983274	0.080727
H35	-1.9098	4.156619	1.748918
H36	-4.26192	4.926004	1.907786
H37	-5.87929	4.345935	0.115954
C38	-2.48279	-1.27242	1.62886
C39	-1.7741	-0.37639	0.766321
C40	-0.96382	0.647784	1.343452
C41	-0.88188	0.735344	2.722269
C42	-1.58725	-0.14178	3.572962
C43	-2.37705	-1.12815	3.035154
H44	-0.24833	1.501958	3.158179
H45	-1.49452	-0.03425	4.649171
H46	-2.92149	-1.81841	3.672989
H47	-5.51946	1.818318	-3.95738
H48	-6.35541	3.213117	-2.05047
C49	-0.7312	2.712219	-0.15036
C50	-0.15531	1.601248	0.524581
C51	1.237535	1.468039	0.529133
C52	2.059519	2.37624	-0.12731
C53	1.497121	3.46531	-0.78709

C54	0.118424	3.630473	-0.78041
F55	1.812263	0.438827	1.162715
F56	3.380382	2.206868	-0.13321
F57	2.280577	4.337287	-1.41776
F58	-0.39983	4.695612	-1.40451

Table S205. Rh^{II}(bisq^{F4})(TFA)₂ thermodynamic values

Temp	298.15	498.15
E_{gas}	-2592.01	-2592.01
E_{solv}	-2592.05	-2592.05
G	-2591.74	-2591.81
ZPE	225.870	225.870
H_{vib}	21.177	54.301
S_{trans}	45.656	48.206
S_{rot}	37.959	39.489
S_{vib}	146.251	231.925
solv	-22.2	-22.2

Table S206. [Rh^{II}(bisq^{F4})(TFA)(TFAH)]⁺ Cartesian coordinates

Atom	x	y	z
Rh1	-1.18212	0.737566	-1.60274
N2	-2.14646	-0.46156	-0.1855
C3	-2.92365	-1.41331	-0.6961
C4	-3.57731	-2.38015	0.084693
C5	-3.39891	-2.35092	1.447964
C6	-5.5218	2.782105	-2.05218
C7	-4.93072	2.142504	-3.11867
C8	-3.61782	1.656292	-2.97688
N9	-2.9146	1.81834	-1.86033
H10	-3.03072	-1.42091	-1.77684
H11	-4.19415	-3.12908	-0.3983
H12	-3.87604	-3.08599	2.089692
H13	-3.12776	1.116361	-3.78097
O14	0.395292	-0.67304	-1.33964
C15	1.638043	-0.69379	-1.29712
O16	2.466444	0.201016	-1.67149

C17	2.271141	-1.97457	-0.70113
F18	3.596148	-1.89485	-0.64354
F19	1.786104	-2.15631	0.538799
F20	1.921725	-3.02543	-1.45676
O21	-0.54044	1.721654	-3.30612
C22	0.59372	2.20948	-3.6062
O23	1.673454	2.104762	-2.99735
C24	0.560404	3.060903	-4.90255
F25	1.770744	3.505413	-5.23044
F26	0.076856	2.322388	-5.91588
F27	-0.25603	4.115145	-4.71941
H28	2.038117	1.031253	-2.18874
C29	-3.43201	2.548375	-0.81674
C30	-4.78283	3.005159	-0.86377
C31	-5.31953	3.67949	0.263516
C32	-4.53686	3.913442	1.369479
C33	-3.17578	3.530921	1.37205
C34	-2.61112	2.864563	0.300025
H35	-6.35087	4.016898	0.231211
H36	-4.94618	4.430615	2.23119
H37	-2.55049	3.798673	2.218587
C38	-1.94921	-0.39597	1.175113
C39	-2.57493	-1.35912	2.030734
C40	-2.34319	-1.31342	3.429075
C41	-1.51615	-0.35612	3.963819
C42	-0.90278	0.592903	3.119844
C43	-1.10863	0.601667	1.749348
H44	-2.82235	-2.05341	4.062428
H45	-1.3273	-0.32254	5.031807
H46	-0.25083	1.343178	3.556749
H47	-5.4571	1.984443	-4.05302
H48	-6.54771	3.134058	-2.11336
C49	-1.12557	2.667062	0.23841
C50	-0.42127	1.648539	0.941413
C51	0.978292	1.718524	0.986762
C52	1.688069	2.756897	0.393256
C53	0.999682	3.761691	-0.28665
C54	-0.38537	3.702533	-0.36047
F55	1.680038	0.748003	1.588744
F56	3.012038	2.77785	0.442001

F57	1.665528	4.748844	-0.86843
F58	-1.02462	4.678357	-1.01102

Table S207. $[\text{Rh}^{\text{II}}(\text{bisq}^{\text{F4}})(\text{TFA})(\text{TFAH})]^+$
thermodynamic values

Temp	298.15	498.15
E_{gas}	-2592.39	-2592.39
E_{solv}	-2592.46	-2592.46
G	-2592.14	-2592.21
ZPE	233.033	233.033
H_{vib}	22.294	56.354
S_{trans}	45.660	48.210
S_{rot}	37.952	39.482
S_{vib}	146.530	232.543
solv	-44.3	-44.3

Table S208. $\text{Rh}^{\text{III}}(\text{bisq}^{\text{F4}})(\text{Me}_{\text{ax}})(\text{H}_{\text{eq}})(\text{TFA}_{\text{eq}})$
Cartesian coordinates

Atom	x	y	z
Rh1	-1.60886	0.124918	-1.98085
N2	-2.26147	-1.06899	0.093891
C3	-2.96408	-2.16417	-0.14133
C4	-3.40417	-3.05745	0.85927
C5	-3.08334	-2.78601	2.164863
C6	-6.21055	1.74332	-1.90065
C7	-5.72937	1.12128	-3.02707
C8	-4.37357	0.738246	-3.07277
N9	-3.51644	0.977352	-2.08697
H10	-3.19374	-2.36936	-1.18165
H11	-3.97548	-3.93663	0.580432
H12	-3.39253	-3.44553	2.971743
H13	-3.9801	0.195692	-3.92337
O14	0.233031	-0.7371	-1.73428
C15	1.272892	-0.36149	-2.40187
O16	1.39661	0.502528	-3.25707
C17	2.53304	-1.12941	-1.91805
F18	3.577742	-0.94773	-2.73835
F19	2.89367	-0.67905	-0.68952

F20	2.319516	-2.45756	-1.81384
H21	-1.17742	0.829831	-3.25908
C22	-3.94371	1.706802	-0.99726
C23	-5.31967	2.054917	-0.84306
C24	-5.74446	2.701713	0.345803
C25	-4.83357	3.018766	1.325097
C26	-3.46087	2.74854	1.130426
C27	-2.99954	2.116984	-0.0107
H28	-6.79699	2.945109	0.462104
H29	-5.15689	3.510433	2.237539
H30	-2.74375	3.068114	1.879976
C31	-1.92518	-0.77455	1.391063
C32	-2.32445	-1.62941	2.471008
C33	-1.9498	-1.32251	3.803175
C34	-1.19164	-0.20873	4.068311
C35	-0.79039	0.634692	3.01169
C36	-1.14398	0.387531	1.695313
H37	-2.26539	-1.9885	4.601918
H38	-0.89348	0.027436	5.085215
H39	-0.18231	1.505974	3.233947
H40	-6.37261	0.889552	-3.86912
H41	-7.25941	2.012011	-1.8094
C42	-1.52706	1.996876	-0.24856
C43	-0.6524	1.307086	0.636424
C44	0.723099	1.494171	0.498512
C45	1.26452	2.326429	-0.48086
C46	0.420487	2.993589	-1.3557
C47	-0.9577	2.824584	-1.23246
F48	1.582271	0.850469	1.300167
F49	2.583557	2.462038	-0.58847
F50	0.91507	3.797015	-2.29354
F51	-1.74938	3.565058	-2.02284
C52	-2.05353	-1.40135	-3.27279
H53	-1.88202	-1.11555	-4.3141
H54	-1.38455	-2.22509	-3.01035
H55	-3.09918	-1.71255	-3.15284

Table S209. $\text{Rh}^{\text{III}}(\text{bisq}^{\text{F4}})(\text{Me}_{\text{ax}})(\text{H}_{\text{eq}})(\text{TFA}_{\text{eq}})$
thermodynamic values

Temp	298.15	498.15
E _{gas}	-2106.30	-2106.30
E _{solv}	-2106.33	-2106.33
G	-2106.00	-2106.06
ZPE	236.204	236.204
H _{vib}	19.292	50.084
S _{trans}	45.233	47.783
S _{rot}	37.171	38.701
S _{vib}	124.662	202.359
solv	-18.2	-18.2

Table S210. Rh^{III}(bisq^{F4})(Me_{eq})(H_{ax})(TFA_{eq})
Cartesian coordinates

Atom	x	y	z
Rh1	-1.48872	0.385518	-1.98862
N2	-1.91608	-1.07719	-0.19152
C3	-2.3697	-2.26358	-0.56957
C4	-2.8255	-3.24871	0.333978
C5	-2.79128	-2.98092	1.679656
C6	-6.21951	1.539358	-1.6877
C7	-5.72532	0.83331	-2.75667
C8	-4.33974	0.594752	-2.83607
N9	-3.4666	1.032831	-1.93267
H10	-2.3498	-2.45838	-1.63522
H11	-3.1875	-4.19668	-0.04972
H12	-3.13571	-3.70955	2.409193
H13	-1.80359	-0.66698	-3.02797
H14	-3.92404	0.012373	-3.64893
O15	0.482166	-0.18273	-1.99144
C16	0.815327	-1.41672	-2.15569
O17	0.123778	-2.39538	-2.40862
C18	2.346557	-1.59223	-1.97186
F19	2.717862	-2.8785	-2.06079
F20	3.03311	-0.9	-2.90639
F21	2.737724	-1.13679	-0.7589
C22	-3.924	1.805937	-0.88351
C23	-5.32393	2.048825	-0.71535
C24	-5.77996	2.79097	0.403583
C25	-4.88431	3.291472	1.316653

C26	-3.5004	3.091061	1.124741
C27	-3.00556	2.372158	0.050966
H28	-6.84744	2.957585	0.518944
H29	-5.23013	3.858811	2.175276
H30	-2.79737	3.527182	1.828018
C31	-1.82879	-0.80066	1.148331
C32	-2.27325	-1.74186	2.13211
C33	-2.16183	-1.43182	3.511061
C34	-1.60296	-0.24203	3.910835
C35	-1.13778	0.676238	2.944568
C36	-1.2481	0.428183	1.587921
H37	-2.50988	-2.1582	4.240937
H38	-1.50369	-0.00612	4.96605
H39	-0.67257	1.601395	3.272555
H40	-6.37489	0.439113	-3.53065
H41	-7.28471	1.721894	-1.57553
C42	-1.51861	2.29893	-0.12873
C43	-0.69331	1.428476	0.629536
C44	0.693937	1.562157	0.536139
C45	1.284413	2.531011	-0.26922
C46	0.480888	3.400114	-0.99721
C47	-0.90201	3.281148	-0.91388
F48	1.499368	0.743577	1.222144
F49	2.60994	2.623375	-0.35217
F50	1.033058	4.332817	-1.77611
F51	-1.65291	4.147214	-1.61312
C52	-1.12362	1.522108	-3.66542
H53	-0.07282	1.382494	-3.93174
H54	-1.75032	1.217659	-4.51099
H55	-1.32238	2.578154	-3.45489

Table S211. Rh^{III}(bisq^{F4})(Me_{eq})(H_{ax})(TFA_{eq})
thermodynamic values

Temp	298.15	498.15
E _{gas}	-2106.31	-2106.31
E _{solv}	-2106.33	-2106.33
G	-2106.00	-2106.07
ZPE	236.134	236.134
H _{vib}	18.792	49.202

S_{trans}	45.233	47.783
S_{rot}	37.193	38.723
S_{vib}	125.002	202.738
solv	-17.1	-17.1

Table S212. Rh^{III}(bisq^{F4})(Me_{eq})(H_{eq})(TFA_{ax})
Cartesian coordinates

Atom	x	y	z
Rh1	-1.49198	0.322671	-1.97471
N2	-2.21125	-1.148	-0.42167
C3	-2.88186	-2.24899	-0.71511
C4	-3.30696	-3.16897	0.270467
C5	-3.0144	-2.91946	1.589912
C6	-6.38061	1.582863	-1.62542
C7	-5.95475	0.867329	-2.71947
C8	-4.571	0.622454	-2.88712
N9	-3.66089	1.084416	-2.04918
H10	-3.07705	-2.41548	-1.77052
H11	-3.85213	-4.05723	-0.03098
H12	-3.32295	-3.60702	2.373129
O13	-2.10713	-1.0183	-3.3689
H14	-4.1928	0.009327	-3.70113
H15	-0.07253	-0.26116	-1.99848
C16	-1.35139	-1.777	-4.10429
O17	-0.14383	-1.88135	-4.16903
C18	-2.26133	-2.68609	-4.97832
F19	-1.55811	-3.43661	-5.83098
F20	-2.98291	-3.52588	-4.18808
F21	-3.14906	-1.9599	-5.69634
C22	-4.05218	1.831085	-0.97494
C23	-5.42856	2.087013	-0.70135
C24	-5.77504	2.821081	0.46176
C25	-4.78919	3.284499	1.303071
C26	-3.42443	3.058147	1.005896
C27	-3.04336	2.345027	-0.11497
H28	-6.82345	3.012041	0.674631
H29	-5.05173	3.84475	2.195378
H30	-2.66252	3.466127	1.66381
C31	-1.8989	-0.87685	0.880327

C32	-2.28743	-1.75223	1.938652
C33	-1.91869	-1.43471	3.269915
C34	-1.18669	-0.29947	3.530647
C35	-0.79997	0.559659	2.477784
C36	-1.14852	0.29577	1.16496
H37	-2.21229	-2.10515	4.073219
H38	-0.89453	-0.05814	4.54814
H39	-0.21191	1.44408	2.705558
H40	-6.65788	0.4716	-3.4449
H41	-7.43791	1.768664	-1.45439
C42	-1.58825	2.222202	-0.48142
C43	-0.70699	1.239243	0.080946
C44	0.694987	1.477192	-0.01629
C45	1.212706	2.606801	-0.60275
C46	0.34492	3.571033	-1.14343
C47	-1.01381	3.370114	-1.08398
F48	1.543588	0.586438	0.512543
F49	2.532146	2.794882	-0.68562
F50	0.854125	4.659788	-1.72341
F51	-1.82263	4.302235	-1.61003
C52	-0.77813	1.521943	-3.50451
H53	-0.7602	0.924052	-4.41717
H54	-1.44711	2.378815	-3.63939
H55	0.23708	1.873971	-3.30101

Table S213. Rh^{III}(bisq^{F4})(Me_{eq})(H_{eq})(TFA_{ax})
thermodynamic values

Temp	298.15	498.15
E_{gas}	-2106.30	-2106.30
E_{solv}	-2106.32	-2106.32
G	-2105.99	-2106.05
ZPE	236.173	236.173
H_{vib}	19.259	50.045
S_{trans}	45.233	47.783
S_{rot}	37.380	38.910
S_{vib}	124.063	201.745
solv	-15.7	-15.7

Table S214. Rh^{III}(bisq^{F4})(TFA)₃ Cartesian coordinates

Atom	x	y	z
Rh1	-1.58207	0.224328	-1.78734
N2	-2.18005	-1.07573	-0.24722
C3	-2.741	-2.24667	-0.51056
C4	-3.10428	-3.1546	0.504928
C5	-2.86158	-2.82532	1.816006
C6	-6.36413	1.373011	-1.69978
C7	-5.81951	0.663597	-2.74083
C8	-4.42285	0.469647	-2.79223
N9	-3.59756	0.974619	-1.88277
H10	-2.88622	-2.47444	-1.56089
H11	-3.56068	-4.09855	0.228742
H12	-3.12605	-3.50324	2.623046
O13	-2.16586	-1.18565	-3.08978
H14	-3.96593	-0.12364	-3.57124
O15	0.138312	-0.85077	-1.61967
C16	1.316429	-0.5612	-2.09388
O17	1.814521	0.508306	-2.37685
C18	2.157608	-1.86788	-2.1926
F19	3.320806	-1.65435	-2.81691
F20	2.434771	-2.33195	-0.949
F21	1.500901	-2.84305	-2.84834
O22	-0.87125	1.579008	-3.11986
C23	-1.4325	1.845626	-4.25639
O24	-2.4093	1.341934	-4.78584
C25	-0.7025	3.037409	-4.93793
F26	-1.2074	3.289295	-6.15125
F27	-0.8667	4.155986	-4.18322
F28	0.614129	2.820187	-5.06362
C29	-1.4758	-1.5501	-4.14599
O30	-0.41298	-1.17035	-4.57112
C31	-2.29664	-2.64826	-4.88379
F32	-1.63584	-3.13708	-5.93128
F33	-2.58502	-3.67683	-4.04882
F34	-3.47456	-2.14654	-5.32089
C35	-4.102	1.770773	-0.88085
C36	-5.50972	1.957157	-0.73161

C37	-5.99729	2.734519	0.34925
C38	-5.12358	3.333844	1.225758
C39	-3.73088	3.205687	1.031616
C40	-3.21386	2.443741	0.000336
H41	-7.07096	2.859169	0.460188
H42	-5.49657	3.933325	2.050231
H43	-3.04847	3.736138	1.689088
C44	-1.90092	-0.71738	1.049364
C45	-2.24202	-1.58948	2.127977
C46	-1.93617	-1.20414	3.457239
C47	-1.30653	-0.00721	3.703403
C48	-0.9635	0.845321	2.632005
C49	-1.25227	0.518032	1.318753
H50	-2.1979	-1.87491	4.2707
H51	-1.06257	0.287563	4.719209
H52	-0.45374	1.781318	2.841322
H53	-6.43571	0.225199	-3.51777
H54	-7.43876	1.508985	-1.61153
C55	-1.74816	2.455759	-0.27799
C56	-0.84373	1.472107	0.232729
C57	0.540623	1.690436	0.040357
C58	1.024561	2.777868	-0.66696
C59	0.126836	3.712938	-1.18258
C60	-1.2383	3.549152	-0.97984
F61	1.41591	0.849467	0.588414
F62	2.325699	2.953708	-0.83832
F63	0.585017	4.758224	-1.85475
F64	-2.07026	4.470315	-1.482

Table S215. Rh^{III}(bisq^{F4})(TFA)₃ thermodynamic values

Temp	298.15	498.15
E _{gas}	-3118.16	-3118.16
E _{solv}	-3118.20	-3118.20
G	-3117.87	-3117.95
ZPE	244.634	244.634
H _{vib}	26.425	65.924
S _{trans}	46.083	48.633
S _{rot}	38.553	40.083

S_{vib}	174.171	274.013
solv	-24.6	-24.6

Table S216. $[\text{Rh}^{\text{III}}(\text{bisq}^{\text{F4}})(\text{TFA})_2(\text{TFAH}_{\text{eq}})]^+$
Cartesian coordinates

Atom	x	y	z
Rh1	-1.19075	0.692771	-1.51136
N2	-2.13875	-0.54286	-0.11169
C3	-2.94164	-1.50005	-0.56922
C4	-3.5851	-2.42155	0.274279
C5	-3.36675	-2.3474	1.628685
C6	-5.57925	2.615962	-2.00883
C7	-5.0172	1.920318	-3.05499
C8	-3.706	1.420444	-2.93045
N9	-2.97802	1.638207	-1.84079
H10	-3.04984	-1.55778	-1.64542
H11	-4.22468	-3.1794	-0.16338
H12	-3.83375	-3.05168	2.311098
H13	-3.25788	0.802693	-3.6983
O14	0.443807	-0.57081	-0.98519
C15	1.633863	-0.82576	-1.25319
O16	2.46112	-0.17504	-1.9618
C17	2.19175	-2.10897	-0.58825
F18	3.463548	-2.32104	-0.90531
F19	2.083624	-1.98221	0.745925
F20	1.454853	-3.15931	-0.97821
O21	-0.54738	1.96451	-3.01357
C22	0.617791	2.308638	-3.3975
O23	1.728583	1.918466	-3.01469
C24	0.570321	3.465919	-4.43302
F25	0.221276	4.59549	-3.78043
F26	1.752679	3.652582	-5.01136
F27	-0.34758	3.223862	-5.37949
H28	2.060317	0.69208	-2.41851
C29	-3.46672	2.415799	-0.81835
C30	-4.8112	2.882688	-0.84769
C31	-5.30086	3.606723	0.270134
C32	-4.47956	3.871905	1.342431
C33	-3.12327	3.472658	1.320064

C34	-2.60906	2.758602	0.254046
H35	-6.32851	3.956602	0.2594
H36	-4.85656	4.426562	2.19544
H37	-2.46839	3.762712	2.13645
C39	-1.90046	-0.42608	1.241288
C40	-2.51001	-1.34804	2.149596
C41	-2.23099	-1.25593	3.537021
C42	-1.37402	-0.29293	4.012308
C43	-0.77779	0.61738	3.116974
C44	-1.0329	0.578822	1.754709
H45	-2.69806	-1.96736	4.210876
H46	-1.14943	-0.22601	5.07163
H47	-0.10338	1.373862	3.505802
H49	-5.56767	1.719704	-3.96704
H50	-6.60316	2.974421	-2.06469
C51	-1.13046	2.534344	0.109261
C52	-0.38185	1.595571	0.886894
C53	1.013849	1.734961	0.937689
C54	1.674226	2.772941	0.291444
C55	0.949567	3.714544	-0.44967
C56	-0.42396	3.5861	-0.53511
F55	1.757782	0.841892	1.598363
F56	2.990697	2.86169	0.349337
F57	1.581989	4.697988	-1.07076
F58	-1.10597	4.501513	-1.21502
O59	-1.71765	-0.59556	-2.95799
C60	-0.86213	-1.0086	-3.86896
O61	0.324164	-0.79446	-3.96082
C62	-1.63596	-1.86132	-4.91558
F63	-2.56268	-1.08635	-5.52344
F64	-0.8178	-2.35389	-5.83556
F65	-2.2803	-2.87771	-4.30931

Table S217. $[\text{Rh}^{\text{III}}(\text{bisq}^{\text{F4}})(\text{TFA})_2(\text{TFAH}_{\text{eq}})]^+$
thermodynamic values

Temp	298.15	498.15
E_{gas}	-3118.55	-3118.55
E_{solv}	-3118.62	-3118.62
G	-3118.27	-3118.36

ZPE	252.122	252.122
H_{vib}	26.401	65.993
S_{trans}	46.087	48.637
S_{rot}	38.568	40.098
S_{vib}	174.436	274.489
solv	-44.0	-44.0

Table S218. [Rh^{III}(bisq^{F4})(κ¹-TFA_{ax})(κ²-TFA_{eq,eq})]⁺
Cartesian coordinates

Atom	x	y	z
Rh1	-1.33742	0.572641	-2.03637
N2	-2.30752	-0.58106	-0.5612
C3	-3.21559	-1.46512	-0.97109
C4	-3.94375	-2.28137	-0.08899
C5	-3.71962	-2.16857	1.261001
C6	-5.479	3.095729	-1.98836
C7	-5.23401	2.210335	-3.01269
C8	-4.01372	1.507224	-3.04277
N9	-3.0715	1.698285	-2.12537
H10	-3.35334	-1.54441	-2.04214
H11	-4.66241	-2.98367	-0.49536
H12	-4.26255	-2.7822	1.974102
H13	-3.80457	0.762614	-3.80167
O14	-0.07728	1.390707	-3.51562
C15	0.781172	0.486355	-3.26007
O16	0.572586	-0.30097	-2.28456
C17	2.120656	0.454615	-4.01039
F18	2.975701	1.24238	-3.31096
F19	2.615269	-0.77702	-4.05477
F20	1.994411	0.945889	-5.23772
C21	-4.48595	3.32592	-1.00363
C22	-3.25254	2.623429	-1.12489
C23	-2.1913	2.872441	-0.22265
C24	-2.39451	3.761484	0.817479
C25	-3.63278	4.423431	0.982344
C26	-4.65343	4.225292	0.080262
H27	-1.58162	3.975784	1.505461
H28	-3.76118	5.112569	1.810728
H29	-5.5942	4.758336	0.180332

C30	-2.75392	-1.2495	1.736259
C31	-2.04169	-0.44755	0.788038
C32	-1.03941	0.446127	1.259688
C33	-0.77551	0.511637	2.619486
C34	-1.48928	-0.26437	3.554463
C35	-2.46289	-1.13042	3.119008
H36	0.003717	1.179972	2.972684
H37	-1.25648	-0.17879	4.610677
H38	-3.01349	-1.74858	3.821656
H39	-5.96546	2.022939	-3.79049
H40	-6.42368	3.627839	-1.92621
C41	-0.82327	2.302774	-0.48865
C42	-0.23244	1.285609	0.337945
C43	1.158021	1.146849	0.347525
C44	1.983034	1.981193	-0.40459
C45	1.429472	2.991497	-1.1992
C46	0.055722	3.145624	-1.22604
F47	1.740569	0.188964	1.070215
F48	3.290041	1.810453	-0.38576
F49	2.218521	3.778426	-1.91427
F50	-0.45787	4.128228	-1.95554
O51	-2.15483	-0.63338	-3.44005
C52	-1.57674	-1.17056	-4.49117
O53	-0.42816	-1.1293	-4.86762
C54	-2.66852	-1.93879	-5.29453
F55	-3.26983	-2.85628	-4.50739
F56	-3.61911	-1.06901	-5.70856
F57	-2.15502	-2.5486	-6.35285

Table S219. [Rh^{III}(bisq^{F4})(κ¹-TFA_{ax})(κ²-TFA_{eq,eq})]⁺
thermodynamic values

Temp	298.15	498.15
E_{gas}	-2591.76	-2591.76
E_{solv}	-2591.83	-2591.83
G	-2591.52	-2591.59
ZPE	227.564	227.564
H_{vib}	21.486	55.202
S_{trans}	45.656	48.206
S_{rot}	37.920	39.450

S_{vib}	139.234	224.382
solv	-43.9	-43.9

Table S220. [Rh^{III}(bisq^{F4})(κ¹-TFA_{eq})(κ²-TFA_{ax,eq})]⁺
Cartesian coordinates

Atom	x	y	z
Rh1	-1.29601	0.627816	-1.95001
N2	-2.27845	-0.51401	-0.46138
C3	-3.2018	-1.38507	-0.8636
C4	-3.92951	-2.1963	0.023606
C5	-3.67709	-2.09549	1.371389
C6	-5.54185	2.883151	-2.01488
C7	-5.21011	2.024413	-3.03877
C8	-3.93336	1.427791	-3.05843
N9	-3.0319	1.691151	-2.11973
H10	-3.35982	-1.45728	-1.9336
H11	-4.66462	-2.88792	-0.37173
H12	-4.21214	-2.71155	2.088266
H13	-3.62396	0.752721	-3.84708
O14	0.298664	-0.8186	-2.07156
C15	-0.35856	-1.4013	-2.97518
O16	-1.50658	-0.94147	-3.30532
C17	0.159088	-2.68468	-3.64704
F18	-0.38983	-3.73786	-3.01386
F19	-0.20273	-2.71278	-4.9301
F20	1.484157	-2.75763	-3.54926
O21	-0.22576	1.636464	-3.34467
C22	-0.71247	1.951416	-4.51604
O23	-1.81413	1.719246	-4.97415
C24	0.359864	2.713056	-5.3441
F25	-0.16715	3.216051	-6.45935
F26	0.878036	3.726207	-4.61908
F27	1.362204	1.879309	-5.6755
C29	-4.58882	3.187445	-1.00986
C30	-3.30555	2.580893	-1.11039
C31	-2.28384	2.88061	-0.17862
C32	-2.56683	3.740616	0.866016
C33	-3.85111	4.316676	1.005684
C34	-4.83828	4.060166	0.080773

H35	-1.78775	3.997201	1.577708
H36	-4.04476	4.985581	1.83773
H37	-5.81575	4.524721	0.170036
C38	-2.69807	-1.18582	1.838323
C39	-2.00179	-0.38182	0.881854
C40	-1.00238	0.526192	1.333761
C41	-0.7107	0.587825	2.6868
C42	-1.39845	-0.20183	3.63117
C43	-2.37863	-1.0706	3.215631
H44	0.065066	1.265258	3.029295
H45	-1.14358	-0.11936	4.682461
H46	-2.91267	-1.69052	3.929399
H47	-5.91071	1.787005	-3.83108
H48	-6.52688	3.338187	-1.96936
C49	-0.8897	2.375133	-0.44064
C50	-0.24322	1.389895	0.392688
C51	1.145441	1.287785	0.351065
C52	1.921556	2.131604	-0.44893
C53	1.322241	3.121666	-1.23099
C54	-0.05476	3.2426	-1.20616
F54	1.784591	0.359292	1.065043
F55	3.229663	1.979826	-0.48076
F56	2.065045	3.916019	-1.98245
F57	-0.61766	4.20279	-1.92354

Table S221. [Rh^{III}(bisq^{F4})(κ¹-TFA_{eq})(κ²-TFA_{ax,eq})]⁺
thermodynamic values

Temp	298.15	498.15
E_{gas}	-2591.76	-2591.76
E_{solv}	-2591.84	-2591.84
G	-2591.52	-2591.59
ZPE	227.314	227.314
H_{vib}	21.680	55.423
S_{trans}	45.656	48.206
S_{rot}	37.868	39.398
S_{vib}	140.586	225.799
solv	-45.6	-45.6

Table S222. $[\text{Rh}^{\text{III}}(\text{bisq}^{\text{F4}})(\text{Me}_{\text{ax}})(\text{TFA}_{\text{eq}})(\text{TFAH}_{\text{eq}})]^+$
Cartesian coordinates

Atom	x	y	z
Rh1	-1.20122	0.512612	-1.49979
N2	-1.75857	-0.9707	-0.135
C3	-1.92207	-2.24113	-0.4899
C4	-2.56793	-3.18402	0.33079
C5	-3.09083	-2.7705	1.53455
C6	-5.60317	2.60487	-1.332
C7	-5.4268	1.340579	-1.83809
C8	-4.14257	0.775936	-1.80222
N9	-3.0797	1.388514	-1.28408
H10	-1.54632	-2.5247	-1.46489
H11	-2.66901	-4.20619	-0.01582
H12	-3.64452	-3.45734	2.167918
H13	-3.97741	-0.20244	-2.22997
O14	0.597106	-0.61249	-1.54258
C15	1.813042	-0.53	-1.80666
O16	2.441183	0.383672	-2.42283
C17	2.687607	-1.68101	-1.25243
F18	3.899969	-1.69276	-1.79504
F19	2.798627	-1.50672	0.07777
F20	2.088661	-2.85837	-1.4811
O21	-0.93912	2.101153	-2.83344
C22	0.06621	2.611194	-3.40734
O23	1.265364	2.273758	-3.37392
C24	-0.24233	3.858508	-4.27969
F25	0.441974	4.913121	-3.81423
F26	0.13413	3.621918	-5.54381
F27	-1.54791	4.160075	-4.27168
H28	1.829048	1.203335	-2.81087
C29	-3.23333	2.631395	-0.69541
C30	-4.51007	3.282224	-0.7439
C31	-4.66601	4.582254	-0.19901
C32	-3.60377	5.217374	0.394669
C33	-2.36206	4.558446	0.485775
C34	-2.15684	3.287005	-0.02862
H35	-5.63956	5.059139	-0.26087
H36	-3.71353	6.214167	0.808911

H37	-1.53882	5.057412	0.986956
C38	-2.1275	-0.56669	1.130503
C39	-2.87849	-1.44025	1.97354
C40	-3.3432	-0.9609	3.227014
C41	-3.03005	0.312772	3.640028
C42	-2.18819	1.128708	2.849462
C43	-1.72485	0.709429	1.616101
H44	-3.92815	-1.62273	3.858924
H45	-3.37981	0.67978	4.59946
H46	-1.86072	2.088182	3.23851
H47	-6.24015	0.779153	-2.2832
H48	-6.57187	3.094919	-1.3678
C49	-0.81895	2.66722	0.180171
C50	-0.63409	1.470106	0.922501
C51	0.679356	1.04679	1.195549
C52	1.791258	1.759092	0.766251
C53	1.608798	2.933649	0.036113
C54	0.320138	3.369362	-0.24789
F55	0.882638	-0.06921	1.901108
F56	3.017889	1.319567	1.026067
F57	2.661033	3.610433	-0.40158
F58	0.187157	4.482294	-0.98059
C59	-1.73606	-0.52187	-3.19249
H60	-2.18756	0.202281	-3.8705
H61	-0.8108	-0.92277	-3.60892
H62	-2.42898	-1.33084	-2.95483

Table S223. $[\text{Rh}^{\text{III}}(\text{bisq}^{\text{F4}})(\text{Me}_{\text{ax}})(\text{TFA}_{\text{eq}})(\text{TFAH}_{\text{eq}})]^+$
thermodynamic values

Temp	298.15	498.15
E _{gas}	-2632.28	-2632.28
E _{solv}	-2632.35	-2632.35
G	-2631.99	-2632.07
ZPE	256.669	256.669
H _{vib}	23.320	59.358
S _{trans}	45.720	48.270
S _{rot}	37.954	39.484
S _{vib}	152.176	243.183
solv	-43.6	-43.6

Table S224. $[\text{Rh}^{\text{III}}(\text{bisq}^{\text{F4}})(\text{Me}_{\text{eq}})(\text{TFA}_{\text{ax}})(\text{TFAH}_{\text{eq}})]^+$
Cartesian coordinates

Atom	x	y	z
Rh1	-1.50502	0.360442	-1.98556
N2	-2.14225	-1.06782	-0.15342
C3	-2.81181	-2.14896	-0.53643
C4	-3.27898	-3.14315	0.345899
C5	-3.02858	-3.00207	1.687568
C6	-6.18192	1.562818	-1.89313
C7	-5.66948	0.930699	-3.00218
C8	-4.29482	0.628259	-3.05254
N9	-3.46013	0.960384	-2.07306
H10	-2.98283	-2.25264	-1.60174
H11	-3.81556	-3.99818	-0.05025
H12	-3.35962	-3.74767	2.40513
O13	-2.08645	-1.17066	-3.22894
H14	-3.87586	0.072065	-3.88016
O15	0.548286	-0.11849	-1.68968
C16	1.547228	-0.51684	-2.31305
O17	1.62551	-1.02662	-3.47881
C18	2.916297	-0.33678	-1.61088
F19	3.308669	0.939551	-1.79258
F20	2.788231	-0.55844	-0.29637
F21	3.838691	-1.15206	-2.10787
H22	0.705079	-1.21922	-3.96076
C23	-1.55718	-1.76968	-4.2238
O24	-0.40705	-1.71216	-4.67119
C25	-2.59109	-2.67526	-4.94653
F26	-2.04224	-3.37039	-5.93286
F27	-3.14997	-3.52573	-4.06436
F28	-3.57346	-1.89641	-5.4534
C29	-3.92688	1.649587	-0.97681
C30	-5.31535	1.936664	-0.83615
C31	-5.76367	2.578097	0.347172
C32	-4.8671	2.924907	1.331665
C33	-3.48636	2.679103	1.158203
C34	-3.00702	2.057563	0.019424
H35	-6.82268	2.789753	0.460441

H36	-5.21065	3.412396	2.238207
H37	-2.7878	3.002932	1.92373
C38	-1.88826	-0.89503	1.186937
C39	-2.31827	-1.86692	2.148136
C40	-2.02232	-1.69328	3.523767
C41	-1.31385	-0.59612	3.94914
C42	-0.88449	0.363541	3.011699
C43	-1.16356	0.245685	1.657708
H44	-2.35963	-2.44718	4.229257
H45	-1.07845	-0.46171	4.999767
H46	-0.32294	1.223518	3.361549
H47	-6.30076	0.637006	-3.83306
H48	-7.24306	1.78132	-1.81502
C49	-1.52827	1.939693	-0.22257
C50	-0.66564	1.286178	0.73084
C51	0.670468	1.647433	0.766513
C52	1.211172	2.618199	-0.09524
C53	0.404478	3.250212	-1.02568
C54	-0.95379	2.92966	-1.05936
F55	1.528076	1.057855	1.601474
F56	2.497464	2.90764	-0.0235
F57	0.89752	4.169714	-1.84838
F58	-1.74112	3.692101	-1.81523
C59	-1.02429	1.489566	-3.65871
H60	-0.01431	1.888594	-3.54025
H61	-1.06068	0.834057	-4.52865
H62	-1.74252	2.302472	-3.763

Table S225. $[\text{Rh}^{\text{III}}(\text{bisq}^{\text{F4}})(\text{Me}_{\text{eq}})(\text{TFA}_{\text{ax}})(\text{TFAH}_{\text{eq}})]^+$
thermodynamic values

Temp	298.15	498.15
E _{gas}	-2632.27	-2632.27
E _{solv}	-2632.33	-2632.33
G	-2631.97	-2632.05
ZPE	257.407	257.407
H _{vib}	22.677	58.292
S _{trans}	45.720	48.270
S _{rot}	38.103	39.633
S _{vib}	150.842	241.789

solv	-39.7	-39.7
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Table S226. Rh^{III}(bisq^{F4})(Me_{ax})(TFA)₂ Cartesian coordinates

Atom	x	y	z
Rh1	-1.7436	0.168075	-1.80652
N2	-2.39758	-0.98805	-0.12256
C3	-3.23186	-2.00059	-0.33234
C4	-3.6281	-2.91319	0.661982
C5	-3.11228	-2.77258	1.924651
C6	-6.43073	1.537703	-1.63676
C7	-5.92251	1.023324	-2.80406
C8	-4.53892	0.761416	-2.89751
N9	-3.6921	1.020149	-1.90718
H10	-3.59435	-2.12034	-1.34409
H11	-4.3089	-3.7167	0.403862
H12	-3.36255	-3.47058	2.718738
H13	-4.09613	0.351354	-3.79772
O14	0.124182	-0.58924	-1.47929
C15	0.986461	-0.87815	-2.40908
O16	0.847473	-1.00896	-3.60992
C17	2.402329	-1.03253	-1.78553
F18	3.261286	-1.59586	-2.64475
F19	2.891854	0.186141	-1.45216
F20	2.387635	-1.78442	-0.66409
O21	-0.96715	1.392877	-3.23656
C22	-1.43712	1.578521	-4.42088
O23	-2.41587	1.084803	-4.96963
C24	-0.60419	2.605133	-5.23765
F25	-0.05575	2.008644	-6.31079
F26	-1.41112	3.592545	-5.68162
F27	0.385441	3.17765	-4.52938
C28	-4.14956	1.675152	-0.78365
C29	-5.54675	1.890666	-0.58553
C30	-5.99677	2.46914	0.628758
C31	-5.09329	2.859211	1.5884
C32	-3.70714	2.735981	1.344982
C33	-3.22213	2.168258	0.180789
H34	-7.06378	2.610989	0.77659

H35	-5.43593	3.304463	2.517275
H36	-3.00105	3.128881	2.070396
C37	-1.91858	-0.7716	1.155981
C38	-2.24285	-1.69263	2.206974
C39	-1.70608	-1.51349	3.506232
C40	-0.88842	-0.44483	3.775268
C41	-0.60749	0.489002	2.759227
C42	-1.10682	0.362514	1.472118
H43	-1.95724	-2.23618	4.277168
H44	-0.46773	-0.30268	4.76566
H45	0.016629	1.346207	2.989557
H46	-6.56019	0.785279	-3.6483
H47	-7.49751	1.70336	-1.51138
C48	-1.75781	2.242489	-0.12787
C49	-0.77172	1.43727	0.499022
C50	0.579046	1.730568	0.26936
C51	0.971953	2.763957	-0.57149
C52	0.007035	3.551795	-1.19184
C53	-1.33519	3.292262	-0.95511
F54	1.537309	1.005971	0.857677
F55	2.262316	3.002201	-0.7889
F56	0.372128	4.545756	-1.9968
F57	-2.24429	4.078104	-1.54949
C58	-2.11206	-1.37083	-3.11275
H59	-1.59894	-1.13318	-4.03847
H60	-1.68936	-2.26909	-2.65817
H61	-3.18911	-1.47536	-3.27137

Table S227. Rh^{III}(bisq^{F4})(Me_{ax})(TFA)₂ thermodynamic values

Temp	298.15	498.15
E_{gas}	-2631.89	-2631.89
E_{solv}	-2631.93	-2631.93
G	-2631.58	-2631.66
ZPE	250.091	250.091
H_{vib}	22.608	58.085
S_{trans}	45.716	48.266
S_{rot}	37.933	39.463
S_{vib}	150.310	240.922

solv	-23.4	-23.4
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Table S228. Rh^{III}(bisq^{F4})(Me_{eq})(TFA)₂ Cartesian coordinates

Atom	x	y	z
Rh1	-1.49391	0.516823	-2.11606
N2	-2.3019	-0.87535	-0.21567
C3	-3.08456	-1.86808	-0.60424
C4	-3.55391	-2.88538	0.254143
C5	-3.17761	-2.85597	1.572737
C6	-6.19661	1.736437	-1.93067
C7	-5.6927	1.162981	-3.07394
C8	-4.31383	0.871736	-3.15027
N9	-3.47443	1.163899	-2.16666
H10	-3.36583	-1.87539	-1.65118
H11	-4.18392	-3.67309	-0.14462
H12	-3.49887	-3.62634	2.269099
O13	-2.06258	-0.90308	-3.44815
H14	-3.88149	0.350613	-3.99766
O15	0.433398	-0.02774	-1.78771
C16	1.261351	-0.52527	-2.65657
O17	1.127926	-0.72437	-3.84796
C18	2.605738	-0.85708	-1.94961
F19	3.518195	-1.32538	-2.80844
F20	3.123239	0.25705	-1.36768
F21	2.4378	-1.77346	-0.97574
C22	-1.6465	-2.13809	-3.44051
O23	-0.89266	-2.71786	-2.68768
C24	-2.41412	-2.92669	-4.5381
F25	-1.89684	-4.14131	-4.7367
F26	-3.70489	-3.08872	-4.12596
F27	-2.45031	-2.28292	-5.71801
C28	-3.93423	1.789752	-1.03282
C29	-5.32226	2.059974	-0.86127
C30	-5.76728	2.620502	0.363618
C31	-4.86567	2.904152	1.362775
C32	-3.4845	2.675609	1.166647
C33	-3.00564	2.135757	-0.01213
H34	-6.82774	2.815123	0.498187

H35	-5.20648	3.325346	2.303535
H36	-2.78283	2.943213	1.950715
C37	-1.93893	-0.80276	1.102551
C38	-2.35581	-1.80094	2.041415
C39	-1.95022	-1.71962	3.397051
C40	-1.15953	-0.67968	3.821989
C41	-0.75517	0.314239	2.908037
C42	-1.12995	0.281205	1.574012
H43	-2.2743	-2.49378	4.087555
H44	-0.84231	-0.61436	4.858162
H45	-0.13283	1.130648	3.259135
H46	-6.33353	0.904134	-3.90966
H47	-7.25859	1.942859	-1.82844
C48	-1.53008	2.020116	-0.25508
C49	-0.65018	1.33516	0.651936
C50	0.704794	1.618462	0.595718
C51	1.244848	2.555595	-0.29967
C52	0.413914	3.223434	-1.1733
C53	-0.9598	2.951916	-1.14735
F54	1.580045	0.972477	1.37235
F55	2.55164	2.78345	-0.30703
F56	0.895173	4.126352	-2.02798
F57	-1.75143	3.762605	-1.86179
C58	-0.97651	1.595912	-3.79666
H59	0.027403	2.002603	-3.66742
H60	-0.9846	0.876515	-4.61236
H61	-1.70753	2.394616	-3.94176

Table S229. Rh^{III}(bisq^{F4})(Me_{eq})(TFA)₂ thermodynamic values

Temp	298.15	498.15
E_{gas}	-2631.88	-2631.88
E_{solv}	-2631.91	-2631.91
G	-2631.57	-2631.64
ZPE	249.532	249.532
H_{vib}	23.441	59.391
S_{trans}	45.716	48.266
S_{rot}	38.004	39.534
S_{vib}	152.658	243.469

solv	-20.3	-20.3
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Table S230. $[\text{Rh}^{\text{IV}}(\text{bisq}^{\text{F4}})(\text{Me}_{\text{ax}})(\text{TFA})_2]^+$ Cartesian coordinates

Atom	x	y	z
Rh1	-1.75618	0.155831	-1.80276
N2	-2.41804	-0.96583	-0.129
C3	-3.27653	-1.9668	-0.33442
C4	-3.66609	-2.87533	0.65797
C5	-3.11696	-2.74876	1.912741
C6	-6.43643	1.512308	-1.62289
C7	-5.94044	0.950974	-2.77762
C8	-4.56501	0.676626	-2.86503
N9	-3.70651	0.969106	-1.88625
H10	-3.6648	-2.0725	-1.33818
H11	-4.36388	-3.66743	0.411777
H12	-3.36042	-3.45156	2.704457
H13	-4.14369	0.223961	-3.75272
O14	0.065373	-0.62446	-1.51915
C15	0.961942	-0.71921	-2.46664
O16	0.832281	-0.48683	-3.65555
C17	2.355402	-1.10693	-1.89457
F18	3.145378	-1.57963	-2.85494
F19	2.9211	-0.00634	-1.36523
F20	2.233114	-2.03176	-0.93184
O21	-1.02376	1.361741	-3.1751
C22	-1.42093	1.53349	-4.42455
O23	-2.39339	1.038897	-4.95499
C24	-0.50062	2.544583	-5.15657
F25	0.767762	2.118531	-5.1527
F26	-0.90375	2.717586	-6.41258
F27	-0.55652	3.728611	-4.51225
C28	-4.1506	1.659679	-0.77354
C29	-5.54823	1.889315	-0.58597
C30	-5.99836	2.513975	0.605579
C31	-5.09471	2.928632	1.555631
C32	-3.71033	2.783336	1.320904
C33	-3.22384	2.171425	0.177802
H34	-7.06393	2.672923	0.742738

H35	-5.43556	3.411527	2.465583
H36	-3.00438	3.197943	2.034161
C37	-1.90874	-0.75544	1.141866
C38	-2.22706	-1.68602	2.187165
C39	-1.65733	-1.53238	3.476492
C40	-0.81324	-0.48149	3.739058
C41	-0.54124	0.460127	2.729108
C42	-1.07522	0.361172	1.450551
H43	-1.90193	-2.25966	4.244696
H44	-0.3667	-0.35914	4.720246
H45	0.099866	1.304491	2.95924
H46	-6.58389	0.691246	-3.61056
H47	-7.50095	1.692924	-1.50141
C48	-1.75879	2.251051	-0.13034
C49	-0.75924	1.452019	0.489756
C50	0.587372	1.774969	0.263933
C51	0.964413	2.836811	-0.5517
C52	-0.01369	3.622186	-1.15905
C53	-1.35244	3.326856	-0.93642
F54	1.558244	1.049004	0.825822
F55	2.247113	3.095847	-0.76248
F56	0.334437	4.63329	-1.94179
F57	-2.27343	4.101828	-1.51775
C58	-2.07735	-1.40167	-3.13261
H59	-1.5323	-1.15524	-4.03828
H60	-1.66274	-2.28179	-2.64114
H61	-3.146	-1.5019	-3.3161

Table S231. $[\text{Rh}^{\text{IV}}(\text{bisq}^{\text{F4}})(\text{Me}_{\text{ax}})(\text{TFA})_2]^+$ thermodynamic values

Temp	298.15	498.15
E_{gas}	-2631.60	-2631.60
E_{solv}	-2631.68	-2631.68
G	-2631.33	-2631.41
ZPE	249.927	249.927
H_{vib}	23.154	59.062
S_{trans}	45.716	48.266
S_{rot}	37.907	39.437
S_{vib}	150.011	240.708

solv	-49.2	-49.2
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Table S232. $[\text{Rh}^{\text{IV}}(\text{bisq}^{\text{F4}})(\text{Me}_{\text{eq}})(\text{TFA})_2]^+$ Cartesian coordinates

Atom	x	y	z
Rh1	-1.53989	0.436195	-2.03199
N2	-2.32702	-0.96947	-0.32166
C3	-3.06541	-1.995	-0.72905
C4	-3.56659	-2.98522	0.134751
C5	-3.28885	-2.88677	1.476485
C6	-6.24765	1.63881	-1.76079
C7	-5.80176	0.887373	-2.82509
C8	-4.43136	0.584101	-2.92284
N9	-3.54716	1.021069	-2.03178
H10	-3.27447	-2.04845	-1.7909
H11	-4.14849	-3.80399	-0.27307
H12	-3.64814	-3.63255	2.180061
O13	-2.01943	-0.96682	-3.42079
H14	-4.03922	-0.04749	-3.71281
O15	0.377612	0.136131	-1.9231
C16	1.245479	-0.32767	-2.82634
O17	1.176127	-0.17624	-4.02044
C18	2.47268	-0.94091	-2.10862
F19	3.288282	-1.52841	-2.97485
F20	3.137855	0.063714	-1.48967
F21	2.095783	-1.82446	-1.17563
C22	-1.38769	-2.11442	-3.52183
O23	-0.4268	-2.52089	-2.90844
C24	-2.13309	-3.00093	-4.56155
F25	-1.5368	-4.17795	-4.70561
F26	-3.40166	-3.21154	-4.12004
F27	-2.208	-2.39258	-5.75318
C28	-3.94635	1.803737	-0.97247
C29	-5.3272	2.113814	-0.7931
C30	-5.72049	2.874072	0.3377
C31	-4.77931	3.305972	1.243424
C32	-3.41139	3.017608	1.040853
C33	-2.9808	2.282115	-0.04965
H34	-6.77231	3.106467	0.474768

H35	-5.07834	3.885289	2.110729
H36	-2.67954	3.394725	1.749089
C37	-2.04424	-0.82891	1.01635
C38	-2.51936	-1.8	1.957267
C39	-2.20252	-1.67174	3.333462
C40	-1.43649	-0.62013	3.774474
C41	-0.96357	0.334517	2.852906
C42	-1.25547	0.259937	1.498551
H43	-2.56684	-2.42531	4.025543
H44	-1.18499	-0.52027	4.825182
H45	-0.3527	1.155066	3.215306
H46	-6.48135	0.509874	-3.58056
H47	-7.3025	1.873416	-1.6489
C48	-1.50364	2.092859	-0.28514
C49	-0.69176	1.29705	0.600346
C50	0.680862	1.513037	0.614086
C51	1.293671	2.485729	-0.18667
C52	0.523827	3.298517	-1.01229
C53	-0.85235	3.115268	-1.02759
F54	1.488525	0.762545	1.36217
F55	2.603816	2.62248	-0.16561
F56	1.092479	4.234791	-1.76076
F57	-1.58722	3.982224	-1.72465
C58	-1.4109	1.675466	-3.72913
H59	-0.34178	1.718161	-3.93216
H60	-1.93475	1.128021	-4.50774
H61	-1.85722	2.637874	-3.49712

Table S233. $[\text{Rh}^{\text{IV}}(\text{bisq}^{\text{F4}})(\text{Me}_{\text{eq}})(\text{TFA})_2]^+$ thermodynamic values

Temp	298.15	498.15
E_{gas}	-2631.59	-2631.59
E_{solv}	-2631.66	-2631.66
G	-2631.32	-2631.39
ZPE	249.726	249.726
H_{vib}	23.434	59.387
S_{trans}	45.716	48.266
S_{rot}	37.997	39.527
S_{vib}	153.080	243.899

solv	-45.5	-45.5
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Table S234. $[\text{Rh}^{\text{I-III}}(\text{bisq}^{\text{F4}})(\text{Me}_{\text{ax}}\cdots\text{H}_{\text{eq}})(\text{TFA}_{\text{eq}})]^{\ddagger}$
Cartesian coordinates

Atom	x	y	z
Rh1	-1.54267	0.335941	-2.03904
N2	-2.31771	-1.03919	0.175207
C3	-3.04883	-2.09999	-0.10435
C4	-3.49542	-3.03081	0.860909
C5	-3.14356	-2.82735	2.172396
C6	-6.22566	1.717796	-1.85616
C7	-5.75087	1.12731	-3.00278
C8	-4.38686	0.783099	-3.08724
N9	-3.51557	1.01968	-2.1137
H10	-3.30363	-2.24363	-1.15311
H11	-4.09432	-3.88286	0.555996
H12	-3.45485	-3.51808	2.952119
H13	-3.99966	0.284276	-3.9666
O14	0.329903	-0.40804	-1.69862
C15	1.299676	-0.38416	-2.55282
O16	1.334046	0.043507	-3.69614
C17	2.575843	-1.00912	-1.92367
F18	3.622226	-0.95743	-2.75842
F19	2.92207	-0.35515	-0.78924
F20	2.37213	-2.30459	-1.59709
H21	-1.30582	0.411286	-3.58963
C28	-3.95168	1.675219	-0.98064
C29	-5.32659	2.006524	-0.79984
C30	-5.73744	2.602567	0.420348
C31	-4.81373	2.872348	1.402688
C32	-3.44499	2.592226	1.193479
C33	-2.99868	2.008896	0.021321
H34	-6.7882	2.840009	0.561325
H35	-5.12685	3.325722	2.338421
H36	-2.72412	2.854998	1.960436
C37	-1.95874	-0.80989	1.473412
C38	-2.35449	-1.70253	2.521886
C39	-1.9514	-1.45499	3.858248
C40	-1.17139	-0.36213	4.149944

C41	-0.77387	0.520211	3.122895
C42	-1.15166	0.331245	1.803276
H43	-2.26442	-2.14393	4.638542
H44	-0.85343	-0.17023	5.17037
H45	-0.15075	1.372445	3.373328
H46	-6.40366	0.903179	-3.83941
H47	-7.27654	1.971279	-1.74663
C48	-1.54464	1.810637	-0.24421
C49	-0.66433	1.249412	0.746752
C50	0.691226	1.492476	0.632829
C51	1.23684	2.277938	-0.40174
C52	0.415563	2.803637	-1.36785
C53	-0.97336	2.540213	-1.32506
F48	1.569827	0.948151	1.487305
F49	2.554201	2.478345	-0.44553
F50	0.90427	3.573605	-2.34
F51	-1.74892	3.368655	-2.06251
C58	-1.70906	-1.03774	-3.71121
H59	-2.39039	-0.84179	-4.54349
H60	-0.74493	-1.35644	-4.10204
H61	-2.13546	-1.83628	-3.09157

Table S235. $[\text{Rh}^{\text{I-III}}(\text{bisq}^{\text{F4}})(\text{Me}_{\text{ax}}\cdots\text{H}_{\text{eq}})(\text{TFA}_{\text{eq}})]^{\ddagger}$
thermodynamic values

Temp	298.15	498.15
E_{gas}	-2106.29	-2106.29
E_{solv}	-2106.31	-2106.31
G	-2105.98	-2106.05
ZPE	234.522	234.522
H_{vib}	19.302	49.974
S_{trans}	45.233	47.783
S_{rot}	37.175	38.705
S_{vib}	124.878	202.287
solv	-17.5	-17.5

Table S236. $[\text{Rh}^{\text{I-III}}(\text{bisq}^{\text{F4}})(\text{Me}_{\text{eq}}\cdots\text{H}_{\text{ax}})(\text{TFA}_{\text{eq}})]^{\ddagger}$
Cartesian coordinates

Atom	x	y	z
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Rh1	-1.47988	0.280572	-1.72892
N2	-1.62542	-1.11844	0.031646
C3	-1.82174	-2.38882	-0.30425
C4	-2.32735	-3.35229	0.597531
C5	-2.64562	-2.96953	1.877713
C6	-6.2185	1.365281	-1.13917
C7	-5.78771	0.314306	-1.90981
C8	-4.40509	0.079499	-2.02617
N9	-3.47458	0.816563	-1.42187
H10	-1.54906	-2.64899	-1.3232
H11	-2.46537	-4.37352	0.25835
H12	-3.05981	-3.67737	2.591433
H13	-1.76401	-0.04557	-3.22548
H14	-4.03313	-0.73762	-2.63308
O15	0.501608	-0.18651	-2.0152
C16	0.836919	-1.35709	-2.42989
O17	0.137322	-2.32504	-2.71488
C18	2.37957	-1.483	-2.55232
F19	2.748638	-2.69725	-2.98841
F20	2.877374	-0.569	-3.41347
F21	2.973385	-1.28084	-1.3545
C28	-3.87461	1.876593	-0.6297
C29	-5.26746	2.181029	-0.47898
C30	-5.67102	3.286333	0.311969
C31	-4.7337	4.07258	0.934795
C32	-3.36383	3.768549	0.795546
C33	-2.91651	2.694478	0.0444
H34	-6.7324	3.497891	0.408085
H35	-5.03652	4.924512	1.53575
H36	-2.6284	4.392051	1.29526
C37	-1.8582	-0.72797	1.325628
C38	-2.40883	-1.63294	2.286429
C39	-2.67701	-1.1799	3.603451
C40	-2.38316	0.112878	3.965417
C41	-1.78765	0.990824	3.031699
C42	-1.5212	0.597458	1.733885
H43	-3.10438	-1.8761	4.320533
H44	-2.5822	0.460009	4.974848
H45	-1.51128	1.993391	3.344868
H46	-6.48143	-0.33427	-2.43365

H47	-7.27594	1.588396	-1.02716
C48	-1.43772	2.46824	-0.00949
C49	-0.78797	1.518194	0.813619
C50	0.608565	1.478691	0.822695
C51	1.374927	2.352577	0.060796
C52	0.737783	3.30333	-0.72954
C53	-0.64968	3.357709	-0.7467
F48	1.247357	0.579572	1.584253
F49	2.705995	2.287561	0.08521
F50	1.457249	4.146897	-1.47397
F51	-1.23707	4.26743	-1.54724
C58	-1.42415	1.365108	-3.61618
H59	-0.53313	1.131464	-4.20035
H60	-2.30119	1.409217	-4.26964
H61	-1.30514	2.349688	-3.15603

Table S237. $[\text{Rh}^{\text{I-III}}(\text{bisq}^{\text{F4}})(\text{Me}_{\text{eq}}\cdots\text{H}_{\text{ax}})(\text{TFA}_{\text{eq}})]^{\ddagger}$
thermodynamic values

Temp	298.15	498.15
E_{gas}	-2106.30	-2106.30
E_{solv}	-2106.32	-2106.32
G	-2105.99	-2106.06
ZPE	235.006	235.006
H_{vib}	19.360	49.941
S_{trans}	45.233	47.783
S_{rot}	37.253	38.783
S_{vib}	125.215	202.388
solv	-17.0	-17.0

Table S238. $[\text{Rh}^{\text{I-III}}(\text{bisq}^{\text{F4}})(\text{Me}_{\text{eq}}\cdots\text{H}_{\text{eq}})(\text{TFA}_{\text{ax}})]^{\ddagger}$
Cartesian coordinates

Atom	x	y	z
Rh1	-1.37786	0.375383	-1.91247
N2	-2.34736	-0.93155	-0.44667
C3	-3.12109	-1.96059	-0.75636
C4	-3.64191	-2.8383	0.220282
C5	-3.33547	-2.63151	1.544562
C6	-6.4606	1.570311	-1.57962

C7	-6.07844	0.890305	-2.71182
C8	-4.69645	0.698066	-2.95983
N9	-3.75581	1.166564	-2.16565
H10	-3.3106	-2.10682	-1.81499
H11	-4.26972	-3.66596	-0.09274
H12	-3.71612	-3.29304	2.318402
O13	-1.98353	-0.99585	-3.30842
H14	-4.34986	0.123642	-3.81697
H15	0.111463	0.341804	-2.3973
C22	-1.25368	-1.78246	-4.03279
O23	-0.04498	-1.90938	-4.09829
C24	-2.18238	-2.67137	-4.90839
F25	-1.4951	-3.49649	-5.70377
F26	-2.9902	-3.43277	-4.12411
F27	-2.98849	-1.91462	-5.6888
C28	-4.10622	1.855497	-1.04375
C29	-5.4729	2.072579	-0.6914
C30	-5.77752	2.755068	0.51377
C31	-4.76033	3.197281	1.328654
C32	-3.40716	2.992031	0.968175
C33	-3.06397	2.332907	-0.19764
H34	-6.81784	2.918529	0.782933
H35	-4.98925	3.716564	2.254534
H36	-2.62318	3.367535	1.619624
C37	-2.02003	-0.70332	0.86247
C38	-2.49665	-1.54678	1.907836
C39	-2.09139	-1.28173	3.240004
C40	-1.24342	-0.23129	3.506652
C41	-0.7759	0.598792	2.462808
C42	-1.15765	0.386239	1.14989
H43	-2.44785	-1.92658	4.038287
H44	-0.92336	-0.03384	4.525278
H45	-0.10401	1.418099	2.699528
H46	-6.81114	0.490118	-3.4054
H47	-7.5115	1.724263	-1.34721
C48	-1.60913	2.212906	-0.59588
C49	-0.69032	1.292497	0.047367
C50	0.702712	1.640507	0.050425
C51	1.174374	2.792672	-0.51471
C52	0.275559	3.693554	-1.13511

C53	-1.05996	3.401784	-1.17504
F48	1.574158	0.814716	0.650095
F49	2.480236	3.080474	-0.51957
F50	0.761834	4.807206	-1.69236
F51	-1.89526	4.279121	-1.75358
C58	-0.18447	1.343957	-3.47216
H59	0.11034	0.657222	-4.26435
H60	-1.00897	1.972912	-3.81926
H61	0.65812	1.984179	-3.20294

Table S239. $[\text{Rh}^{\text{I-III}}(\text{bisq}^{\text{F4}})(\text{Me}_{\text{eq}}\cdots\text{H}_{\text{eq}})(\text{TFA}_{\text{ax}})]^{\ddagger}$
thermodynamic values

Temp	298.15	498.15
E_{gas}	-2106.28	-2106.28
E_{solv}	-2106.31	-2106.31
G	-2105.98	-2106.04
ZPE	234.589	234.589
H_{vib}	19.347	50.001
S_{trans}	45.233	47.783
S_{rot}	37.369	38.899
S_{vib}	125.184	202.547
solv	-14.9	-14.9

Table S240. $[\text{Rh}^{\text{I-III}}(\text{bisq}^{\text{F4}})(\text{H}_{\text{ax}}\cdots\text{TFA}_{\text{eq}})(\text{Me}_{\text{eq}})]^{\ddagger}$
Cartesian coordinates

Atom	x	y	z
Rh1	-1.36264	0.567092	-1.86249
N2	-1.99376	-0.76606	-0.05748
C3	-2.61845	-1.87783	-0.42434
C4	-3.05778	-2.87217	0.474364
C5	-2.81422	-2.70002	1.813929
C6	-6.09027	1.569292	-1.90407
C7	-5.45968	1.088823	-3.02627
C8	-4.05919	0.937581	-3.01534
N9	-3.2945	1.259171	-1.97174
H10	-2.77367	-2.00115	-1.49121
H11	-3.56492	-3.75217	0.093013
H12	-3.12061	-3.44439	2.544321

H13	-1.29755	-0.79734	-2.95181
H14	-3.53692	0.512865	-3.86376
O15	0.588059	-0.39035	-1.86428
C16	0.511165	-1.36181	-2.63944
O17	-0.53664	-1.70205	-3.29156
C18	1.742572	-2.25638	-2.85531
F19	1.453279	-3.52624	-2.50887
F20	2.102986	-2.24693	-4.15069
F21	2.785631	-1.85062	-2.12314
C28	-3.89015	1.85414	-0.87487
C29	-5.31257	1.968655	-0.78843
C30	-5.90346	2.482961	0.394606
C31	-5.11681	2.896294	1.442155
C32	-3.71023	2.855607	1.324267
C33	-3.08775	2.359678	0.192546
H34	-6.98676	2.548208	0.45071
H35	-5.56763	3.28689	2.349535
H36	-3.09619	3.248956	2.128778
C37	-1.7538	-0.5595	1.279688
C38	-2.144	-1.53378	2.257635
C39	-1.85057	-1.32734	3.629024
C40	-1.18794	-0.1937	4.029856
C41	-0.81599	0.775466	3.075276
C42	-1.0921	0.629474	1.725297
H43	-2.15315	-2.08361	4.348463
H44	-0.9512	-0.03267	5.077199
H45	-0.30068	1.671589	3.406979
H46	-6.01552	0.795264	-3.91043
H47	-7.17199	1.660525	-1.85815
C48	-1.60259	2.501626	0.067025
C49	-0.67453	1.724987	0.804929
C50	0.680564	2.062258	0.735232
C51	1.137153	3.129709	-0.03036
C52	0.22555	3.899188	-0.74275
C53	-1.12672	3.583293	-0.68036
F48	1.595834	1.345142	1.408622
F49	2.44151	3.415594	-0.08262
F50	0.648356	4.931095	-1.47921
F51	-1.98564	4.352387	-1.37053
C58	-0.79369	1.633299	-3.5281

H59	-0.41526	0.980771	-4.32598
H60	-1.61331	2.234889	-3.94252
H61	0.020297	2.315386	-3.24327

Table S241. $[\text{Rh}^{\text{I-III}}(\text{bisq}^{\text{F4}})(\text{H}_{\text{ax}}\cdots\text{TFA}_{\text{eq}})(\text{Me}_{\text{eq}})]^{\ddagger}$
thermodynamic values

Temp	298.15	498.15
E_{gas}	-2106.28	-2106.28
E_{solv}	-2106.30	-2106.30
G	-2105.98	-2106.04
ZPE	233.743	233.743
H_{vib}	18.724	48.956
S_{trans}	45.233	47.783
S_{rot}	37.341	38.872
S_{vib}	125.092	202.378
solv	-12.4	-12.4

Table S242. $[\text{Rh}^{\text{I-III}}(\text{bisq}^{\text{F4}})(\text{H}_{\text{eq}}\cdots\text{TFA}_{\text{ax}})(\text{Me}_{\text{eq}})]^{\ddagger}$
Cartesian coordinates

Atom	x	y	z
Rh1	-1.66915	0.466382	-2.00723
N2	-2.59397	-0.86684	-0.48891
C3	-3.48065	-1.82047	-0.72415
C4	-3.94797	-2.69709	0.280515
C5	-3.46304	-2.56472	1.560684
C6	-6.62864	1.821213	-1.46874
C7	-6.32253	1.336276	-2.71792
C8	-4.96085	1.160472	-3.06425
N9	-3.96093	1.454193	-2.25616
H10	-3.82817	-1.90519	-1.74973
H11	-4.67588	-3.46079	0.026771
H12	-3.79622	-3.22538	2.35692
O13	-1.84646	-1.23372	-3.41809
H14	-4.68912	0.75426	-4.03656
H15	-0.20899	-0.50536	-2.09422
C22	-0.76036	-1.84955	-3.37833
O23	0.244026	-1.53307	-2.66332
C24	-0.57547	-3.09404	-4.26452

F25	-0.10275	-4.12266	-3.54041
F26	-1.73187	-3.47499	-4.82497
F27	0.302388	-2.82703	-5.24682
C28	-4.24052	1.965096	-1.01788
C29	-5.58279	2.149309	-0.56715
C30	-5.81425	2.631328	0.746927
C31	-4.75231	2.921683	1.570857
C32	-3.4227	2.760306	1.112687
C33	-3.14994	2.288209	-0.15685
H34	-6.83782	2.763279	1.08852
H35	-4.92722	3.287544	2.578424
H36	-2.59987	3.016739	1.773368
C37	-2.09509	-0.7131	0.775862
C38	-2.5057	-1.55815	1.848418
C39	-1.92863	-1.37086	3.129591
C40	-0.98369	-0.38862	3.318125
C41	-0.58668	0.447961	2.249607
C42	-1.13133	0.310972	0.984117
H43	-2.23373	-2.01764	3.947877
H44	-0.53269	-0.24781	4.29597
H45	0.160582	1.213983	2.430668
H46	-7.09796	1.077753	-3.43209
H47	-7.66151	1.954907	-1.15661
C48	-1.73049	2.189475	-0.66648
C49	-0.75443	1.237992	-0.14028
C50	0.634869	1.610053	-0.21917
C51	1.054689	2.798706	-0.74089
C52	0.106073	3.726688	-1.24378
C53	-1.22204	3.420367	-1.21136
F48	1.557663	0.75331	0.258382
F49	2.355638	3.10598	-0.81968
F50	0.547313	4.877013	-1.76802
F51	-2.10453	4.310303	-1.69769
C58	-0.74845	1.541457	-3.51789
H59	-0.76924	0.910815	-4.41474
H60	-1.30933	2.458187	-3.72851
H61	0.290649	1.801075	-3.29226

Table S243. $[\text{Rh}^{\text{I-III}}(\text{bisq}^{\text{F4}})(\text{H}_{\text{eq}}\cdots\text{TFA}_{\text{ax}})(\text{Me}_{\text{eq}})]^{\ddagger}$
thermodynamic values

Temp	298.15	498.15
E_{gas}	-2106.28	-2106.28
E_{solv}	-2106.29	-2106.29
G	-2105.97	-2106.03
ZPE	233.611	233.611
H_{vib}	19.140	49.815
S_{trans}	45.233	47.783
S_{rot}	37.349	38.879
S_{vib}	122.642	200.045
solv	-12.0	-12.0

Table S244. $[\text{Rh}^{\text{I-III}}(\text{bisq}^{\text{F4}})(\text{H}_{\text{eq}}\cdots\text{TFA}_{\text{eq}})(\text{Me}_{\text{ax}})]^{\ddagger}$
Cartesian coordinates

Atom	x	y	z
Rh1	-1.52192	0.269501	-1.98676
N2	-2.34854	-1.15673	0.438062
C3	-3.08927	-2.22314	0.215047
C4	-3.59758	-3.05887	1.238268
C5	-3.29755	-2.75205	2.542917
C6	-6.16454	1.721417	-1.92444
C7	-5.6553	1.14908	-3.0654
C8	-4.29501	0.780332	-3.10783
N9	-3.45706	0.979899	-2.09533
H10	-3.29836	-2.44874	-0.82905
H11	-4.20448	-3.92165	0.982278
H12	-3.65932	-3.36721	3.363308
H13	-3.88013	0.291255	-3.97993
O14	0.523049	-0.44387	-1.97643
C15	1.082082	-0.01478	-3.00512
O16	0.524807	0.720804	-3.89062
C17	2.576473	-0.31825	-3.19997
F18	2.932824	-0.25933	-4.48906
F19	3.29469	0.595674	-2.51677
F20	2.883643	-1.53415	-2.72861
H21	-0.59075	0.814602	-3.42781
C28	-3.92562	1.620644	-0.96635
C29	-5.30044	1.972687	-0.82951
C30	-5.74559	2.558372	0.383501
C31	-4.85353	2.805006	1.40068

C32	-3.4824	2.50831	1.235742
C33	-3.00451	1.927771	0.07427
H34	-6.79716	2.810847	0.489761
H35	-5.19296	3.254144	2.329411
H36	-2.78549	2.756403	2.029353
C37	-2.03967	-0.8302	1.725224
C38	-2.49466	-1.61857	2.830622
C39	-2.12948	-1.26221	4.153285
C40	-1.32999	-0.16597	4.374227
C41	-0.87634	0.614502	3.288774
C42	-1.21861	0.317638	1.97942
H43	-2.48454	-1.8711	4.980999
H44	-1.04066	0.107929	5.384528
H45	-0.24267	1.473343	3.486153
H46	-6.27991	0.956764	-3.93127
H47	-7.21441	1.991224	-1.84824
C48	-1.54456	1.718661	-0.14806
C49	-0.69387	1.148403	0.86448
C50	0.66935	1.365667	0.775388
C51	1.251644	2.139459	-0.24619
C52	0.45251	2.701629	-1.21113
C53	-0.94075	2.457406	-1.20346
F48	1.520748	0.807893	1.65393
F49	2.577309	2.30829	-0.27136
F50	0.976021	3.476826	-2.16423
F51	-1.68679	3.31437	-1.94235
C58	-1.97385	-1.29309	-3.26541
H59	-1.98887	-0.99827	-4.32221
H60	-1.22431	-2.08187	-3.13429
H61	-2.96079	-1.70049	-3.009

Table S245. $[\text{Rh}^{\text{III}}(\text{bisq}^{\text{F4}})(\text{H}_{\text{eq}}\cdots\text{TFA}_{\text{eq}})(\text{Me}_{\text{ax}})]^{\ddagger}$ thermodynamic values

Temp	298.15	498.15
E_{gas}	-2106.28	-2106.28
E_{solv}	-2106.30	-2106.30
G	-2105.97	-2106.03
ZPE	233.800	233.800
H_{vib}	19.095	49.753

S_{trans}	45.233	47.783
S_{rot}	37.279	38.809
S_{vib}	122.299	199.661
solv	-11.5	-11.5

Table S246.

$[\text{Rh}^{\text{III}}(\text{bisq}^{\text{F4}})(\text{Me}_{\text{ax}}\cdots\text{H}\cdots\text{TFA}_{\text{eq}})(\text{TFA}_{\text{eq}})]^{+\ddagger}$ Cartesian coordinates

Atom	x	y	z
Rh1	-2.71496	0.324676	-1.44661
N2	-1.52048	-0.73002	0.019483
C3	-1.78259	-2.02383	0.191383
C4	-1.06099	-2.86924	1.047833
C5	-0.0064	-2.34248	1.751062
C11	-6.1919	-0.31133	1.933233
C12	-6.35328	-0.92448	0.712975
C13	-5.3974	-0.70446	-0.29802
N14	-4.35258	0.098661	-0.1392
H15	-2.60178	-2.42947	-0.38352
H16	-1.33869	-3.91437	1.120751
H17	0.59739	-2.96092	2.4088
H23	-5.48713	-1.21434	-1.24784
O28	-1.03858	0.796836	-2.56621
C29	-0.45903	-0.15023	-3.17487
O30	-0.83589	-1.34079	-3.19253
C31	0.861065	0.216227	-3.89335
F32	0.936337	-0.39566	-5.07288
F33	0.961958	1.537166	-4.07202
F34	1.885323	-0.19088	-3.12041
O35	-3.91184	1.383894	-2.71037
C36	-3.75759	1.31669	-4.00853
O37	-3.00685	0.61202	-4.654
C38	-4.73256	2.30345	-4.70979
F39	-4.63352	2.214092	-6.03432
F40	-6.004	2.038717	-4.35362
F41	-4.44859	3.5694	-4.34067
H42	-2.13491	-1.27232	-2.74623
C43	-3.42238	-1.53842	-2.6758
H44	-3.16009	-1.96201	-3.65512

H45	-3.62651	-2.35164	-1.9814
H46	-4.30838	-0.94918	-2.88624
C41	0.301188	-0.96825	1.62247
C42	-0.49815	-0.15471	0.752478
C35	-0.20063	1.240858	0.666954
C44	0.876651	1.746861	1.382717
C45	1.673743	0.937841	2.214342
C46	1.384291	-0.39809	2.338995
H50	1.103574	2.804895	1.307874
H51	2.504304	1.379556	2.754757
H52	1.978176	-1.04078	2.981722
C47	-4.2195	0.803925	1.037789
C48	-5.10692	0.578033	2.130326
C49	-4.87706	1.258957	3.353603
C50	-3.8273	2.140349	3.471972
C51	-2.99841	2.413682	2.360017
C52	-3.18775	1.770198	1.149866
H55	-5.54737	1.078216	4.18848
H56	-3.65185	2.661216	4.407698
H57	-2.22169	3.16783	2.447159
H53	-6.89067	-0.48967	2.745455
H54	-7.18467	-1.59136	0.514729
C55	-1.00026	2.181163	-0.14773
C56	-2.44079	2.216956	-0.07901
C57	-3.11196	3.207386	-0.85917
C58	-2.44298	4.062165	-1.71803
C59	-1.05399	3.973447	-1.79805
C60	-0.35188	3.048547	-1.01787
F59	-4.4205	3.349215	-0.72862
F60	-3.09589	4.965304	-2.43237
F61	-0.39742	4.754387	-2.63165
F62	0.972499	3.000589	-1.18851

Table S247.

$[\text{Rh}^{\text{III}}(\text{bisq}^{\text{F4}})(\text{Me}_{\text{eq}}\cdots\text{H}\cdots\text{TFA}_{\text{ax}})(\text{TFA}_{\text{eq}})]^{++}$
thermodynamic values

Temp	298.15	498.15
E _{gas}	-2632.21	-2632.21
E _{solv}	-2632.29	-2632.29

G	-2631.93	-2632.00
ZPE	254.420	254.420
H _{vib}	23.030	59.045
S _{trans}	45.720	48.270
S _{rot}	37.926	39.456
S _{vib}	148.401	239.351
solv	-46.9	-46.9

Table S248.

$[\text{Rh}^{\text{III}}(\text{bisq}^{\text{F4}})(\text{Me}_{\text{eq}}\cdots\text{H}\cdots\text{TFA}_{\text{ax}})(\text{TFA}_{\text{eq}})]^{++}$ Cartesian coordinates

Atom	x	y	z
Rh1	-1.40106	0.109334	-1.55358
N2	-1.85527	-1.30276	-0.05686
C3	-1.97407	-2.60227	-0.29229
C4	-2.40105	-3.50429	0.704022
C5	-2.72739	-3.02633	1.952472
C11	-6.21795	1.324082	-1.51893
C12	-5.7082	0.206397	-2.13001
C13	-4.32326	-0.01892	-2.07584
N14	-3.45866	0.791829	-1.46464
H15	-1.74767	-2.93486	-1.29802
H16	-2.48043	-4.55761	0.460127
H17	-3.08815	-3.6953	2.728472
H22	-3.90193	-0.89086	-2.55802
O27	0.387452	-0.86319	-1.6489
C28	1.542622	-0.35551	-1.97009
O29	1.862845	0.81132	-2.10237
C30	2.57277	-1.49978	-2.19189
F31	2.718653	-2.22569	-1.06795
F32	2.135503	-2.32264	-3.16791
F33	3.761483	-1.01536	-2.54561
H34	-0.49113	1.90182	-4.05412
H35	-0.75238	0.530964	-3.65008
O36	-1.91716	-1.36886	-2.9083
C37	-1.31935	-1.37017	-4.0295
O38	-0.6292	-0.43605	-4.48292
C39	-1.54124	-2.64404	-4.87562
F40	-0.81413	-2.62405	-5.98377

F41	-1.21932	-3.72136	-4.14506
F42	-2.84488	-2.71545	-5.19725
C43	-0.8918	1.762621	-3.03643
H44	-1.82811	2.318188	-3.02153
H45	-0.11017	2.182248	-2.41277
C41	-5.34408	2.212093	-0.84992
C42	-3.93909	1.920936	-0.82512
C35	-3.07439	2.837202	-0.14931
C44	-3.61491	3.975099	0.43605
C45	-4.99375	4.252654	0.408942
C46	-5.84544	3.381211	-0.22307
H50	-2.95116	4.668676	0.941129
H51	-5.37049	5.150841	0.886861
H52	-6.91343	3.573443	-0.26137
C47	-2.08771	-0.8059	1.197436
C48	-2.57822	-1.6455	2.238023
C49	-2.87313	-1.06495	3.49781
C50	-2.66289	0.279234	3.707292
C51	-2.11312	1.08684	2.685065
C52	-1.81743	0.560742	1.439934
H55	-3.25786	-1.69706	4.292526
H56	-2.887	0.723525	4.671667
H57	-1.89385	2.130092	2.893609
H53	-7.28134	1.544253	-1.5409
H54	-6.33873	-0.50116	-2.65604
C55	-1.6141	2.629526	-0.05026
C56	-1.05935	1.385029	0.423736
C57	0.360914	1.305806	0.536039
C58	1.205249	2.355579	0.204978
C59	0.639354	3.544724	-0.24497
C60	-0.7519	3.665675	-0.37862
F59	0.907148	0.216604	1.055552
F60	2.514014	2.245958	0.341779
F61	1.415352	4.55879	-0.57144
F62	-1.20824	4.824381	-0.86763

Table S249.

$[\text{Rh}^{\text{III}}(\text{bisq}^{\text{F4}})(\text{Me}_{\text{eq}}\cdots\text{H}\cdots\text{TFA}_{\text{eq}})(\text{TFA}_{\text{ax}})]^{+\ddagger}$
thermodynamic values

Temp	298.15	498.15
E_{gas}	-2632.21	-2632.21
E_{solv}	-2632.28	-2632.28
G	-2631.93	-2632.00
ZPE	254.557	254.557
H_{vib}	23.076	59.038
S_{trans}	45.720	48.270
S_{rot}	38.094	39.624
S_{vib}	149.301	240.119
solv	-44.1	-44.1

Table S250.

$[\text{Rh}^{\text{III}}(\text{bisq}^{\text{F4}})(\text{Me}_{\text{eq}}\cdots\text{H}\cdots\text{TFA}_{\text{eq}})(\text{TFA}_{\text{ax}})]^{+\ddagger}$ Cartesian coordinates

Atom	x	y	z
Rh1	-2.61143	0.084708	-1.47559
N2	-1.51123	-1.05502	-0.01882
C3	-1.83586	-2.33815	0.113477
C4	-1.20722	-3.20191	1.027844
C5	-0.20648	-2.70781	1.826897
C11	-5.99295	0.151895	2.019269
C12	-6.16254	-0.65589	0.918869
C13	-5.21051	-0.61482	-0.11813
N14	-4.16591	0.206053	-0.09007
H15	-2.61168	-2.70428	-0.54717
H16	-1.52242	-4.23803	1.07564
H17	0.305978	-3.34266	2.544044
H23	-5.27402	-1.28269	-0.96944
O28	-0.95277	-0.23262	-2.68794
C29	-0.91185	0.435956	-3.76207
O30	-1.7704	1.26815	-4.13235
C31	0.366379	0.287677	-4.61656
F32	1.218777	1.263068	-4.23155
F33	0.95114	-0.89399	-4.41811
F34	0.095364	0.438098	-5.91007
H35	-4.14136	1.546191	-3.89918
H36	-2.83073	1.106031	-3.33321
O37	-3.43137	-1.64196	-2.10595
C38	-3.45145	-2.04103	-3.36014

O39	-3.0452	-1.48552	-4.35307
C40	-4.16295	-3.42381	-3.41657
F41	-4.20876	-3.89449	-4.6553
F42	-3.51957	-4.31353	-2.63181
F43	-5.42577	-3.29952	-2.94871
C44	-4.10958	1.126589	-2.88197
H45	-4.7813	0.273789	-2.91409
H46	-4.47759	1.902011	-2.21725
C41	-3.99071	1.065458	0.969057
C42	-4.88814	1.037553	2.07801
C43	-4.64389	1.8942	3.18168
C36	-3.56323	2.74545	3.174004
C45	-2.7071	2.797493	2.051202
C46	-2.90706	1.979252	0.95357
H49	-5.32564	1.868669	4.026642
H50	-3.37512	3.400714	4.018246
H51	-1.88875	3.511616	2.041023
C48	-0.50004	-0.52501	0.754497
C49	0.179464	-1.3512	1.70664
C50	1.232898	-0.81118	2.486687
C51	1.620042	0.497017	2.325581
C52	0.964113	1.306472	1.377639
C53	-0.08475	0.828454	0.605835
H55	1.73442	-1.45643	3.201323
H56	2.432303	0.910858	2.913808
H57	1.288539	2.33405	1.246684
H53	-6.99934	-1.34037	0.837324
H54	-6.69558	0.122359	2.847286
C55	-0.70505	1.757549	-0.37382
C56	-2.07069	2.177477	-0.28311
C57	-2.49237	3.225692	-1.14429
C58	-1.65987	3.801579	-2.08524
C59	-0.33661	3.357038	-2.18175
C60	0.123703	2.352947	-1.33481
F59	-3.73416	3.701219	-1.02192
F60	-2.09836	4.759671	-2.88951
F61	0.465667	3.885748	-3.08573
F62	1.394189	1.965445	-1.46652

Table S251.

$[\text{Rh}^{\text{III}}(\text{bisq}^{\text{F4}})(\text{Me}_{\text{eq}}\cdots\text{H}\cdots\text{TFA}_{\text{eq}})(\text{TFA}_{\text{ax}})]^{+\ddagger}$
thermodynamic values

Temp	298.15	498.15
E _{gas}	-2632.22	-2632.22
E _{solv}	-2632.29	-2632.29
G	-2631.93	-2632.01
ZPE	254.663	254.663
H _{vib}	22.974	58.937
S _{trans}	45.720	48.270
S _{rot}	38.033	39.563
S _{vib}	148.393	239.210
solv	-43.2	-43.2

Table S252. $[\text{Rh}^{\text{III-I}}(\text{bisq}^{\text{F4}})(\text{Me}_{\text{ax}}\cdots\text{TFA}_{\text{eq}})(\text{TFA}_{\text{eq}})]^{\ddagger}$
Cartesian coordinates

Atom	x	y	z
Rh1	-1.72174	0.194666	-1.87408
N2	-2.37547	-0.88925	-0.14596
C3	-3.18528	-1.91914	-0.36824
C4	-3.59845	-2.83578	0.613877
C5	-3.12642	-2.67556	1.891563
C6	-6.39911	1.511867	-1.74955
C7	-5.89662	0.905031	-2.87476
C8	-4.51208	0.654361	-2.95771
N9	-3.64938	1.005222	-2.00659
H10	-3.53004	-2.04509	-1.38743
H11	-4.25533	-3.65349	0.338485
H12	-3.38944	-3.37149	2.683503
H13	-4.08573	0.145192	-3.81415
O14	0.183258	-0.51946	-1.45029
C15	1.078228	-0.94087	-2.26824
O16	0.98578	-1.28844	-3.44224
C17	2.474899	-0.9793	-1.58723
F18	3.399672	-1.55405	-2.36907
F19	2.895999	0.277383	-1.30973
F20	2.44002	-1.66185	-0.422
O21	-0.99281	1.272456	-3.50263

C22	-1.41701	0.952033	-4.63411
O23	-2.17235	-0.01069	-4.94912
C24	-1.00172	1.853063	-5.82033
F25	-0.43105	1.117708	-6.78716
F26	-2.0974	2.449255	-6.3374
F27	-0.14361	2.809446	-5.45169
C28	-4.10953	1.723692	-0.92039
C29	-5.50982	1.941382	-0.73313
C30	-5.96708	2.581754	0.447217
C31	-5.06901	3.016123	1.391703
C32	-3.68216	2.871853	1.165193
C33	-3.18709	2.25267	0.031348
H34	-7.03545	2.726098	0.58302
H35	-5.41549	3.504094	2.297634
H36	-2.97941	3.284543	1.882669
C37	-1.93918	-0.65641	1.145647
C38	-2.2867	-1.57746	2.192565
C39	-1.80345	-1.38608	3.511208
C40	-1.01177	-0.30532	3.805595
C41	-0.70306	0.62505	2.794965
C42	-1.14741	0.490271	1.487671
H43	-2.07618	-2.10863	4.275277
H44	-0.63293	-0.15125	4.811231
H45	-0.09804	1.490068	3.045259
H46	-6.54036	0.587191	-3.68792
H47	-7.46574	1.680441	-1.62797
C48	-1.71	2.294628	-0.22674
C49	-0.76153	1.555624	0.526469
C50	0.595858	1.846136	0.360972
C51	1.036243	2.833104	-0.51447
C52	0.106425	3.572948	-1.23623
C53	-1.24673	3.310559	-1.07265
F54	1.528263	1.159579	1.036982
F55	2.339467	3.076247	-0.65986
F56	0.514722	4.533396	-2.06773
F57	-2.12604	4.055294	-1.76457
C58	-2.00151	-1.71529	-3.87105
H59	-2.39691	-2.05203	-4.8208
H60	-0.92372	-1.77509	-3.7393
H61	-2.63231	-1.95339	-3.02653

Table S253. $[\text{Rh}^{\text{III-I}}(\text{bisq}^{\text{F4}})(\text{Me}_{\text{ax}}\cdots\text{TFA}_{\text{eq}})(\text{TFA}_{\text{eq}})]^{\ddagger}$
thermodynamic values

Temp	298.15	498.15
E_{gas}	-2631.81	-2631.81
E_{solv}	-2631.85	-2631.85
G	-2631.50	-2631.58
ZPE	248.087	248.087
H_{vib}	23.503	59.304
S_{trans}	45.716	48.266
S_{rot}	38.017	39.547
S_{vib}	153.506	243.943
Solv	-19.5	-19.5

Table S254. $[\text{Rh}^{\text{III-I}}(\text{bisq}^{\text{F4}})(\text{Me}_{\text{eq}}\cdots\text{TFA}_{\text{ax}})(\text{TFA}_{\text{eq}})]^{\ddagger}$
Cartesian coordinates

Atom	x	y	z
Rh1	-1.45014	0.677323	-2.20477
N2	-2.14462	-1.05199	-0.15118
C3	-2.76129	-2.14481	-0.5566
C4	-3.20654	-3.16264	0.319486
C5	-2.97749	-3.01453	1.665205
C6	-6.18201	1.861897	-2.00531
C7	-5.674	1.391638	-3.19257
C8	-4.29537	1.109343	-3.29711
N9	-3.44872	1.286367	-2.2891
H10	-2.90088	-2.2399	-1.63129
H11	-3.7097	-4.03747	-0.07991
H12	-3.29794	-3.77155	2.376669
O13	-1.76216	-1.01932	-3.42909
H14	-3.87258	0.742594	-4.22403
O15	0.440568	-0.05182	-1.84672
C16	1.372201	-0.19929	-2.71983
O17	1.407766	0.119148	-3.9036
C18	2.615019	-0.8661	-2.06796
F19	3.631684	-0.98514	-2.93124
F20	3.048206	-0.12574	-1.01893
F21	2.31876	-2.0969	-1.60182

C22	-1.95254	-0.83718	-4.65346
O23	-1.95832	0.240078	-5.29849
C24	-2.32058	-2.0933	-5.48211
F25	-1.58436	-2.16868	-6.59743
F26	-2.15419	-3.22411	-4.7845
F27	-3.62293	-2.01342	-5.83802
C28	-3.92279	1.807328	-1.10578
C29	-5.30528	2.087284	-0.91448
C30	-5.7353	2.568651	0.348535
C31	-4.82219	2.774603	1.357021
C32	-3.44631	2.529743	1.144036
C33	-2.9859	2.05301	-0.06952
H34	-6.79161	2.769812	0.503227
H35	-5.15214	3.142165	2.323973
H36	-2.73887	2.726112	1.94281
C37	-1.88963	-0.88674	1.178549
C38	-2.29641	-1.86472	2.141278
C39	-1.99992	-1.67503	3.514505
C40	-1.30386	-0.56227	3.921922
C41	-0.885	0.399788	2.977325
C42	-1.1668	0.27157	1.627143
H43	-2.3225	-2.42615	4.230944
H44	-1.0666	-0.41676	4.971509
H45	-0.32437	1.264528	3.318151
H46	-6.30987	1.222055	-4.05457
H47	-7.24234	2.069572	-1.89047
C48	-1.53246	1.854968	-0.35542
C49	-0.6647	1.269713	0.651599
C50	0.673144	1.578767	0.610925
C51	1.241821	2.447548	-0.36058
C52	0.451041	2.98966	-1.32846
C53	-0.94212	2.669044	-1.37937
F54	1.541285	1.030109	1.468971
F55	2.554039	2.681855	-0.32494
F56	0.948331	3.811636	-2.25745
F57	-1.7051	3.622977	-2.0018
C58	-0.93746	1.966633	-4.62225
H59	0.037454	1.54771	-4.38479
H60	-1.16981	2.099065	-5.66867
H61	-1.40118	2.680019	-3.95532

Table S255. $[\text{Rh}^{\text{III-I}}(\text{bisq}^{\text{F4}})(\text{Me}_{\text{eq}}\cdots\text{TFA}_{\text{ax}})(\text{TFA}_{\text{eq}})]^{\ddagger}$
thermodynamic values

Temp	298.15	498.15
E_{gas}	-2631.81	-2631.81
E_{solv}	-2631.84	-2631.84
G	-2631.49	-2631.57
ZPE	247.998	247.998
H_{vib}	22.861	58.271
S_{trans}	45.716	48.266
S_{rot}	38.088	39.619
S_{vib}	152.771	243.221
solv	-15.9	-15.9

Table S256. $[\text{Rh}^{\text{III-I}}(\text{bisq}^{\text{F4}})(\text{Me}_{\text{eq}}\cdots\text{TFA}_{\text{eq}})(\text{TFA}_{\text{ax}})]^{\ddagger}$
Cartesian coordinates

Atom	x	y	z
Rh1	-1.3911	0.689659	-2.1055
N2	-2.0845	-1.01587	-0.02713
C3	-2.69873	-2.11431	-0.42256
C4	-3.14935	-3.1174	0.468355
C5	-2.93151	-2.94811	1.8134
C6	-6.12708	1.771796	-1.94539
C7	-5.60797	1.213544	-3.09045
C8	-4.22432	0.94639	-3.16992
N9	-3.38985	1.244096	-2.18294
H10	-2.83202	-2.2237	-1.49637
H11	-3.64819	-3.99898	0.078761
H12	-3.2561	-3.69481	2.533983
O13	-2.00004	-0.87972	-3.34846
H14	-3.78849	0.440517	-4.0236
O15	0.534742	-0.04321	-1.93768
C16	1.373432	0.367878	-2.77871
O17	1.242308	1.236517	-3.67203
C18	2.798098	-0.21193	-2.59548
F19	3.533345	-0.10116	-3.70578
F20	3.414836	0.479353	-1.60908
F21	2.757701	-1.50092	-2.23624

C22	-1.32347	-1.5781	-4.19763
O23	-0.20164	-1.40556	-4.64798
C24	-2.18468	-2.76704	-4.71104
F25	-1.52097	-3.54473	-5.57135
F26	-2.6074	-3.54894	-3.68772
F27	-3.29249	-2.30193	-5.34028
C28	-3.87591	1.818814	-1.03472
C29	-5.26327	2.081105	-0.86416
C30	-5.70509	2.607539	0.376865
C31	-4.79909	2.855072	1.383142
C32	-3.4192	2.609943	1.19189
C33	-2.94601	2.100402	-0.0026
H34	-6.76446	2.800269	0.521376
H35	-5.13905	3.249976	2.335781
H36	-2.72251	2.828391	1.99411
C37	-1.84472	-0.82626	1.301845
C38	-2.25783	-1.78867	2.277211
C39	-1.97431	-1.57377	3.649467
C40	-1.28644	-0.45103	4.04394
C41	-0.86278	0.496307	3.08687
C42	-1.1314	0.342735	1.736444
H43	-2.30048	-2.31315	4.376527
H44	-1.05964	-0.28635	5.093025
H45	-0.30969	1.369384	3.418482
H46	-6.24189	0.955694	-3.93187
H47	-7.19164	1.968503	-1.85142
C48	-1.4902	1.891062	-0.27734
C49	-0.62642	1.327696	0.747812
C50	0.704504	1.664474	0.725288
C51	1.267341	2.547527	-0.2386
C52	0.482821	3.063104	-1.22642
C53	-0.89925	2.694849	-1.31154
F54	1.573739	1.137301	1.599225
F55	2.568713	2.834892	-0.1641
F56	0.970017	3.92266	-2.12276
F57	-1.67127	3.617821	-1.96506
C58	-0.55	1.864266	-4.4282
H59	-0.75817	0.931867	-4.93394
H60	-1.36785	2.394149	-3.95913
H61	0.181662	2.506335	-4.8984

Table S257. $[\text{Rh}^{\text{III-I}}(\text{bisq}^{\text{F4}})(\text{Me}_{\text{eq}}\cdots\text{TFA}_{\text{eq}})(\text{TFA}_{\text{ax}})]^{\ddagger}$
thermodynamic values

Temp	298.15	498.15
E_{gas}	-2631.81	-2631.81
E_{solv}	-2631.84	-2631.84
G	-2631.49	-2631.57
ZPE	247.912	247.912
H_{vib}	22.914	58.348
S_{trans}	45.716	48.266
S_{rot}	38.084	39.614
S_{vib}	153.420	243.936
solv	-15.9	-15.9

Table S258. $[\text{Rh}^{\text{III-I}}(\text{bisq}^{\text{F4}})(\text{Me}_{\text{ax}}\cdots\text{TFA})(\text{TFA})_2]^{-\ddagger}$
Cartesian coordinates

Atom	x	y	z
Rh1	-1.51899	0.357879	-2.04995
N2	-2.27747	-0.90666	-0.50179
C3	-3.03531	-1.93899	-0.86736
C4	-3.46469	-2.95542	0.00824
C5	-3.07915	-2.90084	1.321175
C6	-6.24173	1.419069	-2.33502
C7	-5.558	1.067203	-3.47382
C8	-4.15642	0.912373	-3.42103
N9	-3.45059	1.118198	-2.31071
H10	-3.30334	-2.03024	-1.91147
H11	-4.05609	-3.76706	-0.40104
H12	-3.35305	-3.67913	2.029462
H13	-3.57752	0.617884	-4.29146
O14	0.377062	-0.34678	-1.56765
C15	1.320435	-0.58547	-2.40994
O16	1.299907	-0.75037	-3.62102
C17	2.689757	-0.6548	-1.67228
F18	3.695575	-1.01103	-2.4919
F19	3.015203	0.549125	-1.13932
F20	2.672025	-1.54805	-0.65313
O21	-0.65163	1.696471	-3.37227

C22	-0.95521	1.866495	-4.60086
O23	-1.78641	1.30171	-5.3124
C24	-0.10325	3.011351	-5.22014
F25	-0.43513	3.255065	-6.50253
F26	-0.28306	4.169894	-4.53614
F27	1.214923	2.729571	-5.19028
C28	-4.09087	1.631753	-1.20092
C29	-5.51548	1.723719	-1.15548
C30	-6.14888	2.130105	0.047581
C31	-5.39739	2.479356	1.144321
C32	-3.98709	2.492054	1.059382
C33	-3.32509	2.093485	-0.08783
H34	-7.23515	2.168916	0.078702
H35	-5.8816	2.787897	2.066758
H36	-3.40325	2.853289	1.90079
C37	-1.94033	-0.77755	0.835107
C38	-2.30753	-1.80121	1.772549
C39	-1.91155	-1.71067	3.130031
C40	-1.19113	-0.62909	3.5712
C41	-0.87397	0.40474	2.670723
C42	-1.23528	0.368723	1.331573
H43	-2.19439	-2.51292	3.80712
H44	-0.87983	-0.55404	4.609267
H45	-0.33414	1.273178	3.033809
H46	-6.07256	0.86284	-4.40693
H47	-7.32681	1.4876	-2.32394
C48	-1.84691	2.312601	-0.19874
C49	-0.87957	1.552829	0.505884
C50	0.45605	1.95897	0.449816
C51	0.857399	3.069601	-0.28448
C52	-0.09259	3.823461	-0.96064
C53	-1.42858	3.452621	-0.89045
F54	1.409095	1.272957	1.100871
F55	2.147264	3.422607	-0.3288
F56	0.277053	4.905126	-1.65311
F57	-2.33001	4.21372	-1.53834
C58	-1.72447	-1.54627	-3.74067
H59	-1.04894	-1.07441	-4.43488
H60	-1.30824	-2.13345	-2.94001
H61	-2.76998	-1.30058	-3.74879

O62	-2.02742	-3.09669	-4.82327
C63	-3.0387	-3.76462	-4.42552
O64	-3.81943	-3.56032	-3.49005
C65	-3.32951	-5.00474	-5.32292
F66	-2.21971	-5.53697	-5.86785
F67	-3.94606	-5.98414	-4.62812
F68	-4.15489	-4.66015	-6.34164

Table S259. $[\text{Rh}^{\text{III-I}}(\text{bisq}^{\text{F4}})(\text{Me}_{\text{ax}}\cdots\text{TFA})(\text{TFA})_2]^{-\dagger}$
thermodynamic values

Temp	298.15	498.15
E_{gas}	-3158.13	-3158.13
E_{solv}	-3158.21	-3158.21
G	-3157.85	-3157.94
ZPE	265.948	265.948
H_{vib}	27.220	67.863
S_{trans}	46.135	48.686
S_{rot}	39.144	40.674
S_{vib}	189.883	294.630
solv	-48.9	-48.9

Table S260. $[\text{Rh}^{\text{III-I}}(\text{bisq}^{\text{F4}})(\text{Me}_{\text{ax}}\cdots\text{TFAH})(\text{TFA})_2]^{-\dagger}$
Cartesian coordinates

Atom	x	y	z
Rh1	-1.92433	0.19726	-1.84677
N2	-2.54944	-0.89478	-0.12522
C3	-3.42431	-1.88111	-0.30788
C4	-3.81085	-2.79664	0.68643
C5	-3.24423	-2.68783	1.930281
C6	-6.49315	1.709971	-1.5926
C7	-5.98949	1.236656	-2.77984
C8	-4.61152	0.95647	-2.87996
N9	-3.75976	1.157372	-1.87529
H10	-3.83428	-1.97666	-1.3036
H11	-4.52369	-3.57653	0.442546
H12	-3.484	-3.38891	2.724855
H13	-4.17658	0.570859	-3.79567
O14	0.03439	-0.80638	-1.79361

C15	0.999671	-1.04697	-2.51854
O16	1.056384	-1.60576	-3.67773
C17	2.40109	-0.65303	-1.98533
F18	3.392381	-1.12727	-2.74373
F19	2.500161	0.687172	-1.94438
F20	2.551931	-1.12899	-0.73806
O21	-1.07941	1.358618	-3.32643
C22	-1.53838	1.602098	-4.50064
O23	-2.49323	1.100214	-5.09105
C24	-0.68795	2.686456	-5.21736
F25	-1.23954	3.065584	-6.37791
F26	-0.55548	3.786023	-4.44327
F27	0.55129	2.217886	-5.47844
C28	-4.20866	1.787481	-0.73182
C29	-5.60504	2.011659	-0.53004
C30	-6.05349	2.553579	0.702138
C31	-5.14949	2.907147	1.674518
C32	-3.76368	2.785983	1.42639
C33	-3.27926	2.249628	0.247067
H34	-7.11995	2.698514	0.851419
H35	-5.49048	3.325453	2.616576
H36	-3.05616	3.158479	2.161135
C37	-2.01945	-0.70736	1.142319
C38	-2.33471	-1.63596	2.192582
C39	-1.75172	-1.49716	3.477532
C40	-0.89402	-0.45838	3.737647
C41	-0.61921	0.483862	2.728084
C42	-1.1616	0.398364	1.453005
H43	-2.00264	-2.22485	4.243928
H44	-0.4403	-0.34373	4.717119
H45	0.031555	1.321732	2.954932
H46	-6.62801	1.04092	-3.63434
H47	-7.55784	1.883515	-1.46107
C48	-1.81656	2.345157	-0.05799
C49	-0.82913	1.502655	0.509613
C50	0.51574	1.800402	0.265822
C51	0.902036	2.878836	-0.52398
C52	-0.06766	3.696607	-1.08933
C53	-1.40848	3.429499	-0.83831
F54	1.488926	1.036425	0.790382

F55	2.194402	3.13207	-0.73513
F56	0.287391	4.735041	-1.84383
F57	-2.32454	4.249406	-1.37772
C58	-2.51684	-1.63363	-3.47161
H59	-2.12471	-0.95133	-4.20838
H60	-1.87663	-2.20974	-2.82495
H61	-3.5751	-1.59117	-3.26842
O62	-2.7736	-3.03933	-4.68389
C63	-1.67619	-3.42979	-5.18739
O64	-0.51793	-3.0466	-4.95092
C65	-1.80405	-4.55818	-6.24643
F66	-3.07702	-4.92144	-6.45811
F67	-1.28144	-4.15372	-7.41659
F68	-1.12253	-5.64528	-5.83596
H69	0.225747	-2.06105	-4.08946

Table S261. $[\text{Rh}^{\text{III}}\text{-(bisq}^{\text{F4}})(\text{Me}_{\text{ax}}\cdots\text{TFAH})(\text{TFA})_2]^{\ddagger}$ thermodynamic values

Temp	298.15	498.15
E_{gas}	-3158.61	-3158.61
E_{solv}	-3158.64	-3158.64
G	-3158.27	-3158.36
ZPE	274.005	274.005
H_{vib}	27.581	68.737
S_{trans}	46.139	48.689
S_{rot}	39.119	40.650
S_{vib}	187.667	292.692
solv	-21.4	-21.4

Table S262. $[\text{Rh}^{\text{III}}\text{-(bisq}^{\text{F4}})(\text{Me}_{\text{ax}}\cdots\text{TFA})(\text{TFA}_{\text{eq}})(\text{TFAH}_{\text{eq}})]^{\ddagger}$ Cartesian coordinates

Atom	x	y	z
Rh1	-1.04457	0.678174	-1.84933
N2	-1.6277	-0.91631	-0.61078
C3	-1.84855	-2.11735	-1.1393
C4	-2.5432	-3.14202	-0.46421
C5	-3.04796	-2.8913	0.786225

C6	-5.5023	2.701863	-1.57836
C7	-5.2386	1.589971	-2.33511
C8	-3.93833	1.056113	-2.31487
N9	-2.93753	1.550712	-1.59123
H10	-1.52828	-2.29603	-2.15881
H11	-2.69928	-4.08235	-0.98036
H12	-3.63692	-3.63439	1.317191
H13	-3.71044	0.198838	-2.93179
O14	0.800658	-0.39958	-1.97422
C15	2.019301	-0.18906	-2.04938
O16	2.63854	0.869456	-2.40479
C17	2.955687	-1.32789	-1.5824
F18	4.096833	-1.34955	-2.27817
F19	3.249493	-1.12191	-0.28177
F20	2.358294	-2.51926	-1.69703
O21	-0.74759	2.341452	-3.1142
C22	0.255126	3.033879	-3.42537
O23	1.472078	2.840555	-3.20497
C24	-0.11388	4.324324	-4.20169
F25	-0.9873	5.060809	-3.48578
F26	0.955288	5.08165	-4.46428
F27	-0.70311	4.003497	-5.37
H28	2.014765	1.70754	-2.73072
C29	-3.17697	2.650508	-0.78571
C30	-4.47531	3.263467	-0.78378
C31	-4.72497	4.417079	0.001066
C32	-3.72923	4.958519	0.773689
C33	-2.46191	4.345723	0.796642
C34	-2.16503	3.211971	0.05544
H35	-5.71668	4.859444	-0.02761
H36	-3.90902	5.845753	1.372516
H37	-1.68426	4.768951	1.424701
C38	-2.00176	-0.68147	0.698258
C39	-2.78395	-1.64451	1.408975
C40	-3.25135	-1.34495	2.713887
C41	-2.92354	-0.15356	3.314443
C42	-2.06979	0.75278	2.650333
C43	-1.59659	0.509471	1.372968
H44	-3.85915	-2.0823	3.23109
H45	-3.27879	0.077226	4.313918

H46	-1.74146	1.650323	3.16597
H47	-5.99195	1.122101	-2.95879
H48	-6.48525	3.164555	-1.57546
C49	-0.78889	2.660238	0.215379
C50	-0.53218	1.41009	0.827229
C51	0.794056	1.04932	1.084779
C52	1.863303	1.875421	0.75248
C53	1.612292	3.101446	0.146327
C54	0.298208	3.478397	-0.11176
F55	1.068466	-0.12488	1.672699
F56	3.116075	1.496168	1.00714
F57	2.623142	3.901022	-0.18909
F58	0.097283	4.659894	-0.71972
C59	-1.51951	-0.43324	-3.91541
H60	-1.72323	0.473713	-4.46426
H61	-0.52319	-0.84471	-3.9279
H62	-2.30738	-0.99815	-3.45329
O63	-1.92236	-1.51155	-5.56547
C64	-2.26337	-2.68994	-5.21711
O65	-2.35545	-3.18564	-4.08644
C66	-2.65172	-3.6184	-6.40436
F67	-2.39072	-3.08415	-7.60844
F68	-1.99488	-4.7927	-6.32342
F69	-3.97682	-3.88845	-6.35521

Table S263. $[\text{Rh}^{\text{III}}\text{-(bisq}^{\text{F4}}\text{)(Me}_{\text{ax}}\cdots\text{TFA)(TFA}_{\text{eq}}\text{)(TFAH}_{\text{eq}}\text{)}]^{\dagger}$
thermodynamic values

Temp	298.15	498.15
E_{gas}	-3158.62	-3158.62
E_{solv}	-3158.65	-3158.65
G	-3158.28	-3158.37
ZPE	273.298	273.298
H_{vib}	27.129	67.819
S_{trans}	46.139	48.689
S_{rot}	39.179	40.709
S_{vib}	188.820	293.657
solv	-21.5	-21.5

Table S264. $[\text{Rh}^{\text{III-I}}(\text{bisq}^{\text{F4}})(\text{Me}_{\text{eq}}\cdots\text{TFA})(\text{TFA})_2]^{-+}$
Cartesian coordinates

Atom	x	y	z
Rh1	-0.99263	0.508459	-2.16878
N2	-2.1269	-1.19508	0.262349
C3	-2.77554	-2.30277	-0.03782
C4	-3.45301	-3.0936	0.925347
C5	-3.42032	-2.70807	2.242279
C6	-5.62306	1.892976	-2.65255
C7	-4.97219	1.332332	-3.72318
C8	-3.61605	0.955556	-3.59916
N9	-2.93844	1.141706	-2.47467
H10	-2.73127	-2.60821	-1.08006
H11	-3.97494	-3.99219	0.610476
H12	-3.92059	-3.2892	3.014145
O13	-1.38139	-0.88482	-3.6774
H14	-3.07852	0.490838	-4.41503
O15	0.855843	-0.20805	-1.6335
C16	1.723506	-0.74039	-2.42704
O17	1.719584	-0.88093	-3.63812
C18	2.947841	-1.23277	-1.6018
F19	3.911769	-1.74647	-2.38376
F20	3.502619	-0.21118	-0.89938
F21	2.600195	-2.18463	-0.70786
C22	-1.3557	-2.16711	-3.62407
O23	-1.22592	-2.92917	-2.67483
C24	-1.60924	-2.75933	-5.04115
F25	-1.51854	-4.10144	-5.05157
F26	-2.86507	-2.44132	-5.45827
F27	-0.7503	-2.28239	-5.95784
C28	-3.54477	1.747013	-1.40146
C29	-4.91611	2.118801	-1.44166
C30	-5.49678	2.693876	-0.2834
C31	-4.73363	2.901934	0.843268
C32	-3.36189	2.562561	0.85775
C33	-2.75723	1.987588	-0.24535
H34	-6.54797	2.968798	-0.30285
H35	-5.17962	3.344971	1.729338
H36	-2.77296	2.763375	1.746031

C37	-2.06519	-0.80278	1.564133
C38	-2.7011	-1.54206	2.61187
C39	-2.57513	-1.1129	3.956832
C40	-1.82418	-0.00046	4.257003
C41	-1.1858	0.726764	3.228689
C42	-1.30022	0.362239	1.896648
H43	-3.06776	-1.68313	4.741322
H44	-1.7147	0.326171	5.287534
H45	-0.59133	1.597899	3.487305
H46	-5.46816	1.173522	-4.67387
H47	-6.66961	2.179893	-2.71856
C48	-1.28868	1.700264	-0.30412
C49	-0.59915	1.140675	0.844227
C50	0.75457	1.349873	0.953484
C51	1.497653	2.133447	0.034331
C52	0.861941	2.717432	-1.01952
C53	-0.52839	2.477626	-1.24228
F54	1.46396	0.806854	1.956482
F55	2.809063	2.293615	0.232776
F56	1.522305	3.506344	-1.87359
F57	-1.15672	3.465353	-1.94151
C58	-0.41484	1.72668	-4.11445
H59	-0.37197	0.801713	-4.66613
H60	-1.32206	2.299325	-4.07147
H61	0.517271	2.192005	-3.82882
O62	-0.26329	2.716768	-6.02063
C63	-1.43125	2.902842	-6.47365
O64	-2.54557	2.639841	-5.99663
C65	-1.46534	3.626387	-7.85812
F66	-0.26965	3.682495	-8.4777
F67	-2.32622	3.023333	-8.71017
F68	-1.89378	4.907203	-7.70904

Table S265. $[\text{Rh}^{\text{III-I}}(\text{bisq}^{\text{F4}})(\text{Me}_{\text{eq}}\cdots\text{TFA})(\text{TFA})_2]^{-+}$
thermodynamic values

Temp	298.15	498.15
E _{gas}	-3158.12	-3158.12
E _{solv}	-3158.19	-3158.19
G	-3157.84	-3157.93

ZPE	265.271	265.271
H_{vib}	27.398	68.135
S_{trans}	46.135	48.686
S_{rot}	39.210	40.740
S_{vib}	190.837	295.822
solv	-47.3	-47.3

Table S266. [Rh^{III}-(bisq^{F4})(Me_{eq}...TFAH)(TFA)₂]⁺
(TFAH H-bonded to TFA_{ax}) Cartesian coordinates

Atom	x	y	z
Rh1	-1.58206	0.958018	-2.20267
N2	-2.423	-0.84254	-0.26334
C3	-3.18693	-1.81495	-0.72128
C4	-3.65557	-2.8875	0.072804
C5	-3.29889	-2.92692	1.397529
C6	-6.30718	1.988673	-1.7845
C7	-5.82392	1.561345	-2.99972
C8	-4.44236	1.319747	-3.15056
N9	-3.57645	1.503357	-2.16235
H10	-3.43451	-1.76932	-1.77608
H11	-4.27287	-3.66013	-0.37396
H12	-3.62725	-3.73558	2.045957
O13	-2.11541	-0.53694	-3.77452
H14	-4.03483	0.943428	-4.08163
O15	0.415052	0.412856	-2.16122
C16	0.783783	-0.82499	-2.16543
O17	0.122753	-1.83661	-2.36325
C18	2.307193	-0.9495	-1.88868
F19	2.671619	-2.2219	-1.69571
F20	3.015907	-0.46057	-2.9262
F21	2.658844	-0.24681	-0.78669
C22	-1.43014	-1.34316	-4.42526
O23	-0.50374	-1.10896	-5.27947
C24	-1.80936	-2.84447	-4.40652
F25	-0.76066	-3.63894	-4.59532
F26	-2.42266	-3.19446	-3.26862
F27	-2.68761	-3.04582	-5.41878
C28	-4.02809	1.952321	-0.94422
C29	-5.40952	2.191858	-0.70653

C30	-5.81372	2.59451	0.592893
C31	-4.87794	2.748912	1.59017
C32	-3.50419	2.525365	1.334919
C33	-3.06961	2.13204	0.083912
H34	-6.86823	2.769399	0.786861
H35	-5.18896	3.051363	2.585551
H36	-2.7828	2.665597	2.133343
C37	-2.06026	-0.85361	1.052327
C38	-2.48144	-1.8996	1.934272
C39	-2.07999	-1.88825	3.293422
C40	-1.27934	-0.87706	3.768681
C41	-0.85494	0.155649	2.906684
C42	-1.22811	0.194953	1.571798
H43	-2.4136	-2.69003	3.946774
H44	-0.96799	-0.86556	4.808891
H45	-0.22022	0.942111	3.300932
H46	-6.48339	1.393486	-3.84409
H47	-7.36847	2.166455	-1.63603
C48	-1.62261	1.946844	-0.252
C49	-0.73511	1.267549	0.678819
C50	0.598923	1.59481	0.649072
C51	1.1453	2.556494	-0.24567
C52	0.33523	3.196621	-1.13393
C53	-1.05628	2.873806	-1.18931
F54	1.48504	0.981848	1.441758
F55	2.453491	2.79594	-0.2054
F56	0.81269	4.114922	-1.97557
F57	-1.84059	3.870122	-1.69094
C58	-0.95756	2.27305	-4.12437
H59	0.040042	1.897689	-3.96341
H60	-1.68046	1.680725	-4.65788
H61	-1.23172	3.257756	-3.78489
O62	-0.35521	3.062481	-5.85115
C63	0.085442	2.174223	-6.62927
O64	0.088519	0.930512	-6.50957
C65	0.764751	2.70404	-7.92242
F66	0.490779	3.997088	-8.14903
F67	2.101715	2.572593	-7.81035
F68	0.364902	1.998225	-8.99412
H69	-0.31659	-0.13127	-5.61256

Table S267. $[\text{Rh}^{\text{III}}(\text{bisq}^{\text{F4}})(\text{Me}_{\text{eq}}\cdots\text{TFAH})(\text{TFA})_2]^{\ddagger}$
(TFAH H-bonded to TFA_{ax}) thermodynamic values

Temp	298.15	498.15
E_{gas}	-3158.61	-3158.61
E_{solv}	-3158.64	-3158.64
G	-3158.26	-3158.35
ZPE	273.385	273.385
H_{vib}	27.520	68.720
S_{trans}	46.139	48.689
S_{rot}	39.058	40.588
S_{vib}	186.409	291.545
solv	-18.7	-18.7

Table S268. $[\text{Rh}^{\text{III}}(\text{bisq}^{\text{F4}})(\text{Me}_{\text{eq}}\cdots\text{TFAH})(\text{TFA})_2]^{\ddagger}$
(TFAH H-bonded to TFA_{eq}) Cartesian coordinates

Atom	x	y	z
Rh1	-1.45898	0.828773	-2.14655
N2	-2.20568	-0.99353	-0.03595
C3	-2.90496	-2.0415	-0.42774
C4	-3.36752	-3.04909	0.452049
C5	-3.07304	-2.93951	1.78883
C6	-6.1892	1.743377	-1.8144
C7	-5.67578	1.237821	-2.98601
C8	-4.28921	1.003151	-3.09679
N9	-3.44791	1.275756	-2.10631
H10	-3.11821	-2.10898	-1.49187
H11	-3.93543	-3.88726	0.061328
H12	-3.40192	-3.69226	2.501175
O13	-2.02125	-0.64145	-3.51321
H14	-3.85386	0.548871	-3.97897
O15	0.590963	0.270714	-2.08244
C16	1.526707	-0.19395	-2.74106
O17	1.820794	-0.09918	-3.98361
C18	2.60352	-0.92851	-1.90605
F19	3.557668	-1.47929	-2.65598
F20	3.176945	-0.02246	-1.08038

F21	2.038135	-1.87788	-1.15217
C22	-1.42444	-1.76123	-3.78024
O23	-0.31881	-2.16633	-3.46623
C24	-2.37537	-2.67322	-4.60615
F25	-1.76274	-3.77069	-5.05555
F26	-3.41844	-3.07073	-3.82702
F27	-2.89833	-2.01783	-5.66323
C28	-3.92649	1.799816	-0.92965
C29	-5.31581	2.032363	-0.73547
C30	-5.74982	2.520394	0.523993
C31	-4.83636	2.760241	1.52538
C32	-3.45513	2.543302	1.311156
C33	-2.99098	2.071281	0.098389
H34	-6.81009	2.69441	0.684323
H35	-5.17102	3.129577	2.489945
H36	-2.75041	2.75679	2.108211
C37	-1.90275	-0.86089	1.287348
C38	-2.3197	-1.83075	2.253263
C39	-1.96922	-1.66826	3.617289
C40	-1.22047	-0.58575	4.013875
C41	-0.80152	0.373054	3.066698
C42	-1.13053	0.266356	1.724994
H43	-2.29641	-2.41366	4.33721
H44	-0.94506	-0.46054	5.056747
H45	-0.20723	1.217946	3.399872
H46	-6.31494	1.000668	-3.82937
H47	-7.25542	1.918316	-1.69979
C48	-1.53537	1.90881	-0.20473
C49	-0.64577	1.274428	0.750802
C50	0.689881	1.597155	0.700731
C51	1.228051	2.526333	-0.22926
C52	0.409001	3.129398	-1.1379
C53	-0.9815	2.803045	-1.17581
F54	1.581864	1.008346	1.506641
F55	2.539977	2.762382	-0.21814
F56	0.887524	4.004343	-2.02667
F57	-1.7742	3.758921	-1.73411
C58	-1.03231	2.091297	-4.15974
H59	-1.26533	1.15448	-4.6343
H60	-1.79184	2.84731	-4.03599

H61	-0.03809	2.302776	-3.80708
O62	-0.5347	2.809482	-5.92804
C63	0.333205	2.056992	-6.45538
O64	0.925596	1.067622	-5.97806
C65	0.651998	2.38954	-7.93948
F66	0.481831	3.694163	-8.20777
F67	1.912259	2.058649	-8.25546
F68	-0.17891	1.687931	-8.73998
H69	1.245051	0.429895	-4.66857

Table S269. $[\text{Rh}^{\text{III}}(\text{bisq}^{\text{F4}})(\text{Me}_{\text{eq}}\cdots\text{TFAH})(\text{TFA})_2]^{\ddagger}$
(TFAH H-bonded to TFA_{eq}) thermodynamic values

Temp	298.15	498.15
E_{gas}	-3158.61	-3158.61
E_{solv}	-3158.64	-3158.64
G	-3158.26	-3158.35
ZPE	273.436	273.436
H_{vib}	27.638	68.844
S_{trans}	46.139	48.689
S_{rot}	39.084	40.615
S_{vib}	187.746	292.895
solv	-18.5	-18.5

Table S270. $[\text{Rh}^{\text{III}}(\text{bisq}^{\text{F4}})(\text{Me}_{\text{eq}}\cdots\text{TFA})(\text{TFA}_{\text{eq}})(\text{TFAH}_{\text{ax}})]^{\ddagger}$ Cartesian coordinates

Atom	x	y	z
Rh1	-1.08667	1.02659	-1.81264
N2	-1.96036	-1.01498	-0.12199
C3	-2.53192	-2.0403	-0.72814
C4	-3.01569	-3.18607	-0.05469
C5	-2.88143	-3.25001	1.309648
C6	-5.82865	1.920254	-2.10963
C7	-5.12637	1.676505	-3.26629
C8	-3.7286	1.482395	-3.21094
N9	-3.06228	1.54094	-2.0637
H10	-2.60988	-1.97057	-1.80947

H11	-3.47391	-3.99051	-0.6211
H12	-3.23087	-4.11338	1.870622
O13	-1.5865	-0.57574	-3.30379
H14	-3.15801	1.271827	-4.11065
O15	0.867665	0.466058	-1.3526
C16	1.781898	-0.09616	-2.0236
O17	1.787615	-0.52381	-3.19038
C18	3.095513	-0.23122	-1.20627
F19	4.038559	-0.90228	-1.87107
F20	3.575531	0.995219	-0.90954
F21	2.85903	-0.87146	-0.0435
H22	0.719389	-0.79202	-4.09347
C23	-1.18497	-1.0684	-4.36744
O24	0.017844	-1.14674	-4.79688
C25	-2.23498	-1.78629	-5.24266
F26	-1.83051	-1.96905	-6.49414
F27	-2.46098	-3.0008	-4.68019
F28	-3.39608	-1.11881	-5.24084
C29	-3.72679	1.834823	-0.89749
C30	-5.1368	2.007123	-0.8741
C31	-5.76769	2.244107	0.374461
C32	-5.01699	2.319071	1.526082
C33	-3.6098	2.182906	1.482914
C34	-2.95735	1.945254	0.287825
H35	-6.84722	2.362177	0.405355
H36	-5.50228	2.498498	2.480613
H37	-3.03582	2.275208	2.398938
C38	-1.82012	-1.05207	1.237388
C39	-2.27007	-2.17564	2.00438
C40	-2.0936	-2.19741	3.410926
C41	-1.48206	-1.14331	4.045801
C42	-1.03345	-0.03282	3.300228
C43	-1.19334	0.042253	1.9254
H44	-2.4454	-3.05993	3.971367
H45	-1.33998	-1.15657	5.122188
H46	-0.55048	0.788499	3.819622
H47	-5.62061	1.615241	-4.22944
H48	-6.90727	2.05083	-2.12707
C49	-1.46757	1.888249	0.171881
C50	-0.67038	1.207189	1.173221

C51	0.632504	1.612792	1.340829
C52	1.229136	2.663533	0.58849
C53	0.510455	3.294719	-0.38031
C54	-0.83746	2.888336	-0.64964
F55	1.449024	0.993605	2.199979
F56	2.498337	2.983754	0.83269
F57	1.030707	4.290128	-1.09763
F58	-1.60486	3.868465	-1.20203
C59	-0.50066	2.344686	-3.62183
H60	0.567517	2.450563	-3.49036
H61	-0.90438	1.497972	-4.14906
H62	-1.12086	3.207717	-3.43574
O63	-0.33199	2.988343	-5.59774
C64	-1.05429	2.23153	-6.31772
O65	-1.75837	1.258492	-5.99309
C66	-1.02872	2.635855	-7.82213
F67	0.232063	2.657589	-8.29615
F68	-1.74027	1.788577	-8.58193
F69	-1.55155	3.870805	-7.98507

Table S271. $[\text{Rh}^{\text{III}}(\text{bisq}^{\text{F4}})(\text{Me}_{\text{eq}}\cdots\text{TFA})(\text{TFA}_{\text{eq}})(\text{TFAH}_{\text{ax}})]^{\ddagger}$
thermodynamic values

Temp	298.15	498.15
E_{gas}	-3158.61	-3158.61
E_{solv}	-3158.64	-3158.64
G	-3158.27	-3158.36
ZPE	273.429	273.429
H_{vib}	26.440	66.778
S_{trans}	46.139	48.689
S_{rot}	39.074	40.604
S_{vib}	187.465	292.429
solv	-18.6	-18.6

Table S272. $[\text{Rh}^{\text{III-II}}(\text{bisq}^{\text{F4}})(\text{Me}_{\text{ax}}\cdots\text{OVCl}_3)(\text{TFA})_2]^{\ddagger}$
Cartesian coordinates

Atom	x	y	z
Rh1	-1.53515	0.006644	-2.04587

N2	-2.27878	-1.14669	-0.39319
C3	-3.12922	-2.13786	-0.64409
C4	-3.56794	-3.06237	0.32014
C5	-3.08296	-2.95311	1.59847
C6	-6.24022	1.26725	-2.13408
C7	-5.67304	0.735868	-3.26709
C8	-4.28267	0.498171	-3.29364
N9	-3.48743	0.794551	-2.27024
H10	-3.48514	-2.23811	-1.66095
H11	-4.25318	-3.84762	0.021355
H12	-3.36243	-3.66409	2.371041
H13	-3.79471	0.072964	-4.16511
O14	0.342949	-0.71378	-1.6235
C15	1.263992	-0.92974	-2.51352
O16	1.179665	-1.04642	-3.7236
C17	2.661734	-1.01026	-1.83961
F18	3.578783	-1.52101	-2.66792
F19	3.066085	0.234555	-1.48799
F20	2.643686	-1.76355	-0.72146
O21	-0.73325	1.237914	-3.46147
C22	-1.10073	1.198039	-4.69518
O23	-1.93615	0.475215	-5.22861
C24	-0.38768	2.258717	-5.57412
F25	0.14105	1.686251	-6.66558
F26	-1.29405	3.175167	-5.98176
F27	0.590911	2.91294	-4.92605
C28	-4.00679	1.446881	-1.17439
C29	-5.41268	1.647517	-1.04674
C30	-5.92324	2.226025	0.143898
C31	-5.06827	2.618778	1.146494
C32	-3.6704	2.498708	0.975041
C33	-3.12847	1.935522	-0.16517
H34	-6.99681	2.360593	0.242139
H35	-5.45789	3.060871	2.058169
H36	-3.00347	2.88842	1.738289
C37	-1.8446	-0.9516	0.903738
C38	-2.21229	-1.88643	1.927146
C39	-1.71803	-1.73126	3.246237
C40	-0.90679	-0.66963	3.560274
C41	-0.58893	0.281159	2.571281

C42	-1.04291	0.176394	1.264887
H43	-1.99828	-2.46501	3.996498
H44	-0.52053	-0.54535	4.566898
H45	0.026009	1.133304	2.840147
H46	-6.26817	0.462119	-4.13096
H47	-7.31418	1.416524	-2.06181
C48	-1.65052	2.012519	-0.40898
C49	-0.67998	1.262443	0.316686
C50	0.669797	1.609141	0.179653
C51	1.081442	2.644545	-0.65171
C52	0.136325	3.378928	-1.36432
C53	-1.20717	3.068827	-1.22355
F54	1.616252	0.931672	0.839361
F55	2.372005	2.931099	-0.77895
F56	0.524735	4.367423	-2.16299
F57	-2.1007	3.807073	-1.8936
C58	-1.65351	-1.95712	-3.45984
H59	-0.90804	-1.63736	-4.1735
H60	-1.35124	-2.58035	-2.6325
H61	-2.68483	-1.67061	-3.59017
O62	-2.05514	-3.69066	-4.4525
V63	-3.50497	-4.07057	-5.0853
Cl64	-3.65469	-6.15955	-5.6313
Cl65	-5.02465	-3.59506	-3.54559
Cl66	-3.85792	-2.76679	-6.79109

Table S273. $[\text{Rh}^{\text{III-III}}(\text{bisq}^{\text{F4}})(\text{Me}_{\text{ax}}\cdots\text{OVCl}_3)(\text{TFA})_2]^{\ddagger}$
thermodynamic values

Temp	298.15	498.15
E _{gas}	-4159.18	-4159.18
E _{solv}	-4159.21	-4159.21
G	-4158.87	-4158.96
ZPE	254.124	254.124
H _{vib}	28.834	69.910
S _{trans}	46.333	48.883
S _{rot}	39.366	40.896
S _{vib}	192.980	296.896
solv	-19.5	-19.5

Table S274. $[\text{Rh}^{\text{III-}}(\text{bisq}^{\text{F4}})(\text{Me}_{\text{ax}}\cdots\text{OVCl}_3)(\text{TFA}_{\text{eq}})(\text{TFAH}_{\text{eq}})]^{++}$
Cartesian coordinates

Atom	x	y	z
Rh1	-1.18738	0.21424	-1.40736
N2	-1.68852	-1.16869	0.07632
C3	-1.82713	-2.46418	-0.19052
C4	-2.47189	-3.35832	0.683996
C5	-3.01675	-2.87009	1.850265
C6	-5.62009	2.274575	-1.37907
C7	-5.41239	0.984503	-1.80178
C8	-4.11974	0.448333	-1.69979
N9	-3.07508	1.109198	-1.20357
H10	-1.4239	-2.80977	-1.13545
H11	-2.5543	-4.40353	0.407924
H12	-3.56949	-3.52021	2.522542
H13	-3.93512	-0.55668	-2.05313
O14	0.593727	-0.93536	-1.56465
C15	1.820823	-0.76832	-1.71428
O16	2.440229	0.254302	-2.14347
C17	2.720677	-1.94501	-1.26588
F18	3.938395	-1.86796	-1.79186
F19	2.813389	-1.90249	0.075759
F20	2.158059	-3.10882	-1.61954
O21	-0.97435	1.626525	-2.93763
C22	0.025348	2.272428	-3.36973
O23	1.237168	2.121291	-3.11879
C24	-0.36831	3.421944	-4.33335
F25	0.697925	4.068708	-4.79633
F26	-1.06056	2.920869	-5.37167
F27	-1.15786	4.29602	-3.6805
H28	1.816698	1.066447	-2.52582
C29	-3.26139	2.38621	-0.70644
C30	-4.55032	3.007024	-0.81507
C31	-4.74224	4.335715	-0.35755
C32	-3.70254	5.031553	0.20692
C33	-2.44687	4.410052	0.350305
C34	-2.20563	3.112714	-0.07806
H35	-5.72479	4.785829	-0.46306

H36	-3.83975	6.049843	0.55568
H37	-1.64061	4.961293	0.823256
C38	-2.08417	-0.68444	1.302952
C39	-2.83078	-1.509	2.197106
C40	-3.32402	-0.94693	3.404447
C41	-3.04275	0.360802	3.723527
C42	-2.20869	1.135597	2.883549
C43	-1.71865	0.634667	1.691804
H44	-3.90715	-1.57118	4.074924
H45	-3.41479	0.791683	4.647442
H46	-1.91183	2.130576	3.201735
H47	-6.20554	0.381977	-2.2292
H48	-6.59581	2.744189	-1.46461
C49	-0.85345	2.546784	0.173826
C50	-0.64419	1.372241	0.948775
C51	0.677508	0.989323	1.238083
C52	1.774808	1.719533	0.799692
C53	1.567115	2.872311	0.043596
C54	0.268568	3.265137	-0.26341
F55	0.905424	-0.10278	1.975508
F56	3.009267	1.318013	1.081055
F57	2.603035	3.565292	-0.40531
F58	0.116145	4.350203	-1.03411
C59	-1.79	-1.17352	-3.41058
H60	-2.17044	-0.24943	-3.81996
H61	-0.73907	-1.40599	-3.49719
H62	-2.41277	-1.78582	-2.7781
O63	-2.24471	-2.26611	-4.89348
V64	-2.55091	-1.72801	-6.41046
Cl65	-4.12443	-0.25906	-6.2157
Cl66	-0.73486	-0.82225	-7.12098
Cl67	-3.1651	-3.36101	-7.6456

Table S275. $[\text{Rh}^{\text{III}}\text{-}^{\text{II}}(\text{bisq}^{\text{F4}})(\text{Me}_{\text{ax}}\cdots\text{OVCl}_3)(\text{TFA}_{\text{eq}})(\text{TFAH}_{\text{eq}})]^{++}$
thermodynamic values

Temp	298.15	498.15
E _{gas}	-4159.57	-4159.57
E _{solv}	-4159.63	-4159.63

G	-4159.28	-4159.37
ZPE	260.940	260.940
H _{vib}	27.750	68.132
S _{trans}	46.336	48.886
S _{rot}	39.412	40.942
S _{vib}	193.855	298.001
solv	-40.4	-40.4

Table S276. $[\text{Rh}^{\text{III}}\text{-}^{\text{II}}(\text{bisq}^{\text{F4}})(\text{Me}_{\text{eq}}\cdots\text{OVCl}_3)(\text{TFA})_2]^{\dagger}$
Cartesian coordinates

Atom	x	y	z
Rh1	-1.27539	0.568286	-2.10902
N2	-2.08413	-0.78311	-0.39022
C3	-2.80935	-1.79797	-0.83345
C4	-3.31182	-2.81868	-0.00087
C5	-3.03282	-2.76816	1.341016
C6	-5.92735	2.001996	-2.18604
C7	-5.40045	1.371284	-3.28767
C8	-4.03569	1.011939	-3.29268
N9	-3.227	1.297349	-2.2805
H10	-3.00183	-1.81612	-1.89784
H11	-3.89025	-3.62532	-0.43736
H12	-3.38594	-3.54052	2.019075
O13	-1.74807	-0.6884	-3.6486
H14	-3.59204	0.451826	-4.10892
O15	0.626482	-0.04333	-1.71103
C16	1.47882	-0.49383	-2.58073
O17	1.364941	-0.63605	-3.78432
C18	2.815224	-0.8388	-1.86814
F19	3.742972	-1.26283	-2.73033
F20	3.30522	0.260464	-1.23822
F21	2.639203	-1.7928	-0.93318
C22	-1.30092	-1.90309	-3.8227
O23	-0.85296	-2.68848	-3.01301
C24	-1.49173	-2.29703	-5.31317
F25	-1.06018	-3.53742	-5.55585
F26	-2.80982	-2.24337	-5.6356
F27	-0.83913	-1.44818	-6.12514
C28	-3.70702	1.983459	-1.18975

C29	-5.0869	2.320213	-1.08807
C30	-5.55508	2.946932	0.095215
C31	-4.68352	3.232492	1.120832
C32	-3.30678	2.942	0.989643
C33	-2.80693	2.336132	-0.1482
H34	-6.60953	3.195389	0.176206
H35	-5.0429	3.707224	2.028535
H36	-2.6237	3.220222	1.786566
C37	-1.8048	-0.68943	0.949649
C38	-2.26896	-1.6932	1.859562
C39	-1.95976	-1.60126	3.239797
C40	-1.2132	-0.55089	3.715205
C41	-0.75625	0.442534	2.826298
C42	-1.03988	0.402784	1.470494
H43	-2.32012	-2.37841	3.908195
H44	-0.96851	-0.47896	4.770242
H45	-0.16365	1.26485	3.21386
H46	-6.01159	1.124144	-4.1484
H47	-6.98116	2.26302	-2.14126
C48	-1.32609	2.18019	-0.33801
C49	-0.49838	1.459802	0.585459
C50	0.866545	1.715712	0.597842
C51	1.459516	2.654064	-0.25541
C52	0.67641	3.357437	-1.15441
C53	-0.69745	3.118946	-1.18648
F54	1.688693	1.033232	1.400134
F55	2.769777	2.848671	-0.21914
F56	1.22101	4.243289	-1.98793
F57	-1.44257	3.913193	-1.96577
C58	-0.46012	1.836351	-4.035
H59	0.483128	2.12241	-3.59636
H60	-0.49599	0.923074	-4.60887
H61	-1.32938	2.464298	-3.9089
O62	0.001898	2.957234	-5.63729
V63	-1.01604	3.234858	-6.88065
Cl64	-0.90145	1.519325	-8.21433
Cl65	-3.03914	3.360904	-6.02707
Cl66	-0.53255	5.097614	-7.87984

Table S277. $[\text{Rh}^{\text{III}}\text{-}^{\text{II}}(\text{bisq}^{\text{F4}})(\text{Me}_{\text{eq}}\cdots\text{OVCl}_3)(\text{TFA})_2]^{\ddagger}$
thermodynamic values

Temp	298.15	498.15
E _{gas}	-4159.17	-4159.17
E _{solv}	-4159.20	-4159.20
G	-4158.86	-4158.95
ZPE	253.727	253.727
H _{vib}	29.052	70.188
S _{trans}	46.333	48.883
S _{rot}	39.321	40.851
S _{vib}	195.297	299.371
solv	-19.9	-19.9

Table S278. $[\text{Rh}^{\text{III}}\text{-}^{\text{II}}(\text{bisq}^{\text{F4}})(\text{Me}_{\text{eq}}\cdots\text{OVCl}_3)(\text{TFA}_{\text{ax}})(\text{TFAH}_{\text{eq}})]^{+\ddagger}$
Cartesian coordinates

Atom	x	y	z
Rh1	-1.27561	0.464201	-2.02406
N2	-1.97187	-1.00785	-0.31498
C3	-2.62113	-2.0784	-0.75722
C4	-3.10541	-3.09794	0.085263
C5	-2.89163	-2.98946	1.437139
C6	-5.95503	1.698959	-2.09718
C7	-5.40449	1.079486	-3.19478
C8	-4.03081	0.769362	-3.19907
N9	-3.22792	1.08506	-2.18623
H10	-2.75721	-2.14573	-1.83124
H11	-3.62523	-3.94592	-0.34665
H12	-3.23728	-3.75684	2.124097
O13	-1.8109	-0.98995	-3.43395
H14	-3.5868	0.222582	-4.0199
O15	0.769146	-0.03435	-1.66917
C16	1.739046	-0.67874	-2.10579
O17	1.855786	-1.32903	-3.19501
C18	3.000995	-0.68566	-1.20706
F19	3.448336	0.577977	-1.08979
F20	2.665078	-1.13338	0.012342
F21	3.966653	-1.44655	-1.7053

H22	1.004428	-1.33306	-3.8257
C23	-1.2318	-1.55577	-4.41616
O24	-0.03696	-1.53723	-4.74457
C25	-2.23406	-2.34959	-5.29615
F26	-1.63666	-2.96539	-6.30634
F27	-2.8721	-3.26109	-4.5361
F28	-3.16031	-1.49683	-5.78868
C29	-3.73473	1.761747	-1.09867
C30	-5.12561	2.054875	-1.00487
C31	-5.61228	2.687779	0.167813
C32	-4.75006	3.022265	1.186717
C33	-3.36538	2.771409	1.060134
C34	-2.85044	2.156962	-0.06683
H35	-6.67332	2.905347	0.244454
H36	-5.1234	3.50593	2.083404
H37	-2.6915	3.088806	1.850197
C38	-1.75264	-0.86023	1.032899
C39	-2.20269	-1.86394	1.951603
C40	-1.94684	-1.72824	3.339579
C41	-1.25903	-0.63947	3.816083
C42	-0.8111	0.350579	2.919742
C43	-1.05027	0.273794	1.555577
H44	-2.29821	-2.50406	4.013039
H45	-1.05407	-0.5341	4.876252
H46	-0.26615	1.203603	3.310595
H47	-6.00489	0.802259	-4.05361
H48	-7.01715	1.922427	-2.0557
C49	-1.36508	2.043079	-0.26361
C50	-0.5287	1.351106	0.682217
C51	0.812013	1.701425	0.759058
C52	1.374217	2.70019	-0.05035
C53	0.587792	3.373698	-0.97347
C54	-0.76603	3.056699	-1.05583
F55	1.649567	1.06124	1.578038
F56	2.662881	2.973794	0.043507
F57	1.111867	4.304191	-1.76531
F58	-1.53115	3.816294	-1.84411
C59	-0.47601	1.844013	-3.94775
H60	0.45343	2.072979	-3.44886
H61	-0.52285	0.964323	-4.57094

H62	-1.355	2.441262	-3.75682
O63	0.011644	2.970413	-5.43552
V64	-1.03143	3.261849	-6.66468
Cl65	-1.41055	1.340692	-7.58917
Cl66	-2.8481	3.990235	-5.71469
Cl67	-0.23333	4.696743	-8.03726

Table S279. [Rh^{III}-
^{II}(bisq^{F4})(Me_{eq}...OVCl₃)(TFA_{ax})(TFAH_{eq})]⁺⁺
thermodynamic values

Temp	298.15	498.15
E _{gas}	-4159.55	-4159.55
E _{solv}	-4159.61	-4159.61
G	-4159.26	-4159.35
ZPE	261.402	261.402
H _{vib}	28.324	69.122
S _{trans}	46.336	48.886
S _{rot}	39.363	40.893
S _{vib}	193.784	297.986
solv	-38.6	-38.6

Table S280. [Rh^{III}-
^{II}(bisq^{F4})(Me_{eq}...OVCl₃)(TFA_{eq})(TFAH_{ax})]⁺⁺
Cartesian coordinates

Atom	x	y	z
Rh1	-1.31493	0.823636	-1.82622
N2	-2.029	-0.84555	-0.25742
C3	-2.73768	-1.83589	-0.78404
C4	-3.18474	-2.95702	-0.0598
C5	-2.87253	-3.03868	1.275159
C6	-6.05981	1.804262	-1.73515
C7	-5.49327	1.359988	-2.90794
C8	-4.1051	1.125755	-2.95994
N9	-3.3092	1.346701	-1.91803
H10	-2.98199	-1.7521	-1.83664
H11	-3.75178	-3.73092	-0.56496
H12	-3.18104	-3.8914	1.873638
O13	-1.67254	-0.38084	-3.55828

H14	-3.63531	0.724064	-3.84985
O15	0.745719	0.536629	-1.63787
C16	1.438279	-0.52039	-1.6032
O17	1.110088	-1.68894	-1.89867
C18	2.884129	-0.34799	-1.06776
F19	3.743256	-1.07383	-1.78227
F20	3.267579	0.937749	-1.10147
F21	2.915002	-0.76486	0.211342
H22	0.120436	-1.98923	-2.67333
C23	-1.44767	-1.56357	-3.89997
O24	-0.60509	-2.3839	-3.43556
C25	-2.40781	-2.14107	-4.96771
F26	-1.84155	-3.10052	-5.68717
F27	-3.47067	-2.65428	-4.3034
F28	-2.85111	-1.17258	-5.7781
C29	-3.83616	1.846871	-0.74886
C30	-5.23728	2.056488	-0.60896
C31	-5.73813	2.502229	0.641874
C32	-4.87816	2.73624	1.690541
C33	-3.48382	2.570575	1.524237
C34	-2.95552	2.13916	0.321541
H35	-6.80707	2.655782	0.755815
H36	-5.26231	3.074924	2.647313
H37	-2.81723	2.807391	2.348098
C38	-1.73797	-0.87683	1.084256
C39	-2.1426	-1.99267	1.889337
C40	-1.81853	-2.03498	3.26942
C41	-1.11812	-1.00571	3.8492
C42	-0.72669	0.100115	3.069292
C43	-1.02565	0.193728	1.717199
H44	-2.13524	-2.89342	3.854761
H45	-0.86629	-1.03213	4.904363
H46	-0.18282	0.909027	3.545271
H47	-6.0918	1.166918	-3.79091
H48	-7.13091	1.966488	-1.6599
C49	-1.47043	2.112388	0.088262
C50	-0.57962	1.385733	0.962944
C51	0.7364	1.807574	1.059234
C52	1.236959	2.899035	0.327198
C53	0.40331	3.606595	-0.52168

C54	-0.93383	3.222685	-0.61736
F55	1.622645	1.149447	1.810515
F56	2.510922	3.225062	0.433274
F57	0.857655	4.635661	-1.22893
F58	-1.75585	4.034106	-1.29111
C59	-0.55447	2.39368	-3.63462
H60	0.435842	2.378436	-3.20475
H61	-0.83529	1.613717	-4.32676
H62	-1.28725	3.115685	-3.30523
O63	0.051572	3.574893	-5.04723
V64	-0.89985	4.017579	-6.29625
Cl65	-1.40038	2.192485	-7.34474
Cl66	-2.67745	4.869086	-5.39564
Cl67	0.106546	5.426077	-7.5513

Table S281. $[\text{Rh}^{\text{III}}\text{-(bisq}^{\text{F4}})(\text{Me}_{\text{eq}}\cdots\text{OVCl}_3)(\text{TFA}_{\text{eq}})(\text{TFAH}_{\text{ax}})]^{+\ddagger}$
thermodynamic values

Temp	298.15	498.15
E _{gas}	-4159.55	-4159.55
E _{solv}	-4159.61	-4159.61
G	-4159.26	-4159.36
ZPE	260.430	260.430
H _{vib}	28.260	69.103
S _{trans}	46.336	48.886
S _{rot}	39.402	40.932
S _{vib}	193.225	297.531
solv	-37.9	-37.9

Table S282.
 $[\text{Rh}^{\text{III}}(\text{bisq}^{\text{F4}})(\text{CH}_2\text{TFA}_{\text{ax}}\cdots\text{H}\cdots\text{TFA}_{\text{eq}})(\text{TFA}_{\text{eq}})]^{+\ddagger}$
Cartesian coordinates

Atom	x	y	z
Rh1	-2.77683	0.323441	-1.50024
N2	-1.59465	-0.75683	-0.06445
C3	-1.88143	-2.04849	0.083505
C4	-1.14893	-2.92682	0.897478
C5	-0.06948	-2.43534	1.587589

C11	-6.25881	-0.33743	1.858321
C12	-6.42794	-0.92815	0.62823
C13	-5.47083	-0.70463	-0.38092
N14	-4.41719	0.085281	-0.20928
H15	-2.72826	-2.42044	-0.47374
H16	-1.4442	-3.96807	0.943267
H17	0.541747	-3.08007	2.212454
H23	-5.5631	-1.21225	-1.33033
O28	-1.08319	0.781804	-2.60875
C29	-0.51642	-0.17752	-3.20593
O30	-0.92098	-1.36323	-3.22586
C31	0.814326	0.151462	-3.92388
F32	0.817745	-0.36587	-5.15017
F33	1.003289	1.472759	-3.99911
F34	1.821808	-0.38618	-3.21449
O35	-3.95433	1.434823	-2.75583
C36	-3.77815	1.388742	-4.05083
O37	-3.05121	0.651848	-4.6909
C38	-4.67711	2.439597	-4.76013
F39	-4.54607	2.367034	-6.08242
F40	-5.96985	2.24332	-4.44201
F41	-4.33036	3.681014	-4.36052
H42	-2.19888	-1.28501	-2.84021
C43	-3.52674	-1.50575	-2.91912
H44	-3.27079	-1.8048	-3.94201
H46	-4.39244	-0.85813	-2.99212
C41	0.254243	-1.06136	1.490929
C42	-0.54875	-0.21431	0.658774
C35	-0.23183	1.177542	0.598655
C44	0.865093	1.651878	1.307974
C45	1.663412	0.811572	2.105567
C46	1.358181	-0.52384	2.200545
H50	1.106382	2.707809	1.25661
H51	2.50886	1.227737	2.643097
H52	1.955685	-1.19096	2.814541
C47	-4.27308	0.765467	0.980819
C48	-5.16154	0.533764	2.069982
C49	-4.91777	1.19068	3.303787
C50	-3.85487	2.054497	3.433945
C51	-3.02437	2.333663	2.324958

C52	-3.22547	1.711011	1.106996
H55	-5.58719	1.005022	4.137946
H56	-3.66915	2.556193	4.377999
H57	-2.2349	3.072978	2.423616
H53	-6.95905	-0.52178	2.667973
H54	-7.26495	-1.58488	0.420499
C55	-1.03315	2.142606	-0.18101
C56	-2.47952	2.161884	-0.12294
C57	-3.15298	3.188249	-0.86476
C58	-2.48489	4.085097	-1.67737
C59	-1.09421	4.000832	-1.75669
C60	-0.38858	3.046109	-1.01459
F58	-4.46102	3.320323	-0.72893
F59	-3.13367	5.025615	-2.34478
F60	-0.43785	4.819047	-2.55128
F61	0.935702	3.016784	-1.18619
O62	-3.89348	-2.65906	-2.14614
C63	-3.66127	-3.88431	-2.67881
O64	-3.18419	-4.12206	-3.75042
C65	-4.11987	-4.95574	-1.66435
F66	-3.42414	-4.81287	-0.50651
F67	-5.4219	-4.80178	-1.37921
F68	-3.90877	-6.17226	-2.14052

Table S283.

$[\text{Rh}^{\text{III}}(\text{bisq}^{\text{F4}})(\text{CH}_2\text{TFA}_{\text{ax}}\cdots\text{H}\cdots\text{TFA}_{\text{eq}})(\text{TFA}_{\text{eq}})]^{+\ddagger}$
thermodynamic values

Temp	298.15	498.15
E_{gas}	-3157.75	-3157.75
E_{solv}	-3157.82	-3157.82
G	-3157.45	-3157.54
ZPE	267.202	267.202
H_{vib}	27.030	67.935
S_{trans}	46.135	48.686
S_{rot}	38.843	40.373
S_{vib}	177.524	280.877
solv	-46.9	-46.9

Table S284.[Rh^{III}(bisq^{F4})(CH₂TFA_{eq}...H...TFA_{ax})(TFA_{eq})]⁺⁺

Cartesian coordinates

Atom	x	y	z
Rh1	-1.415	0.040801	-1.62098
N2	-1.87148	-1.30312	-0.08705
C3	-1.99318	-2.61041	-0.27728
C4	-2.40802	-3.4766	0.754573
C5	-2.71603	-2.95659	1.990921
C11	-6.24552	1.201723	-1.65318
C12	-5.71852	0.073166	-2.22742
C13	-4.33302	-0.13811	-2.14833
N14	-3.48224	0.69785	-1.55314
H15	-1.77845	-2.97807	-1.27288
H16	-2.49234	-4.53716	0.546667
H17	-3.06695	-3.59843	2.793858
H22	-3.90221	-1.0218	-2.59853
O27	0.379523	-0.92947	-1.64845
C28	1.511163	-0.42051	-2.04099
O29	1.765123	0.732024	-2.3451
C30	2.605674	-1.52507	-2.08982
F31	2.773003	-2.07118	-0.87145
F32	2.229581	-2.5012	-2.93975
F33	3.770107	-1.02737	-2.49992
H34	-0.18344	1.794509	-4.06092
H35	-0.851	0.426323	-3.75803
O36	-1.92085	-1.49184	-2.92187
C37	-1.42804	-1.48086	-4.0915
O38	-0.81118	-0.52751	-4.60866
C39	-1.68448	-2.76882	-4.9083
F40	-1.06568	-2.73208	-6.07947
F41	-1.2592	-3.82786	-4.20614
F42	-3.00973	-2.88425	-5.10415
C43	-0.82591	1.666752	-3.17539
H45	-0.2086	2.096387	-2.39531
C41	-5.3875	2.112989	-0.99613
C42	-3.98047	1.839434	-0.95214
C35	-3.13499	2.788382	-0.30031
C44	-3.69304	3.929444	0.259913

C45	-5.07547	4.185949	0.220828
C46	-5.90873	3.289903	-0.40042
H50	-3.04036	4.64768	0.745065
H51	-5.46769	5.090159	0.67414
H52	-6.97813	3.469082	-0.45626
C47	-2.08407	-0.7627	1.153925
C48	-2.5593	-1.5679	2.228455
C49	-2.83102	-0.94694	3.47422
C50	-2.61268	0.402286	3.638664
C51	-2.07979	1.175182	2.581812
C52	-1.80826	0.60894	1.348826
H55	-3.20443	-1.55264	4.294439
H56	-2.81888	0.877501	4.592214
H57	-1.8566	2.224571	2.752049
H53	-7.31005	1.412722	-1.69515
H54	-6.33506	-0.65363	-2.74356
C55	-1.67027	2.619817	-0.21531
C56	-1.07851	1.403905	0.290546
C57	0.346058	1.362231	0.391353
C58	1.16069	2.415344	0.004881
C59	0.560093	3.576314	-0.47902
C60	-0.83695	3.662029	-0.59541
F58	0.922737	0.306707	0.94494
F59	2.47459	2.33784	0.117037
F60	1.307335	4.593311	-0.85275
F61	-1.32372	4.787857	-1.12863
O62	-2.04585	2.408139	-3.36629
C63	-1.97572	3.513166	-4.13471
O64	-1.00654	3.929509	-4.70729
C65	-3.35508	4.208641	-4.14177
F66	-4.33858	3.322789	-4.38714
F67	-3.58444	4.754519	-2.92776
F68	-3.39168	5.167163	-5.05862

Table S285.[Rh^{III}(bisq^{F4})(CH₂TFA_{eq}...H...TFA_{ax})(TFA_{eq})]⁺⁺

thermodynamic values

Temp	298.15	498.15
E _{gas}	-3157.75	-3157.75

E_{solv}	-3157.82	-3157.82
G	-3157.46	-3157.54
ZPE	267.033	267.033
H_{vib}	27.147	68.022
S_{trans}	46.135	48.686
S_{rot}	38.779	40.309
S_{vib}	179.627	282.901
solv	-45.4	-45.4

Table S286.

[Rh^{III}(bisq^{F4})(CH₂TFA_{eq}...H...TFA_{eq})(TFA_{ax})]^{+‡}

Cartesian coordinates

Atom	x	y	z
Rh1	-2.50921	0.00161	-1.40971
N2	-1.27941	-1.25921	-0.25714
C3	-1.25741	-2.57615	-0.42561
C4	-0.56119	-3.42993	0.453235
C5	0.087357	-2.89598	1.542584
C11	-5.61862	0.027308	2.38281
C12	-5.53814	-1.0206	1.498757
C13	-4.63249	-0.93538	0.429133
N14	-3.84009	0.11687	0.225691
H15	-1.83189	-2.96967	-1.25434
H16	-0.57159	-4.49706	0.262887
H17	0.602364	-3.535	2.254072
H23	-4.55503	-1.73597	-0.29672
O28	-1.12725	-0.29823	-2.92673
C29	-1.2123	0.495987	-3.91034
O30	-2.03189	1.438917	-4.01203
C31	-0.14005	0.313153	-5.00913
F32	0.99766	0.885257	-4.56718
F33	0.087663	-0.98346	-5.22977
F34	-0.50924	0.899262	-6.14315
H35	-4.4395	1.338446	-3.64639
H36	-2.9647	1.232556	-3.09079
O37	-3.42689	-1.69272	-2.02875
C38	-3.68743	-1.95313	-3.29225
O39	-3.569	-1.23528	-4.25912
C40	-4.22177	-3.40986	-3.40042

F41	-4.53891	-3.716	-4.65043
F42	-3.2748	-4.27146	-2.9648
F43	-5.30964	-3.56235	-2.61893
C44	-4.24154	1.097068	-2.59291
H45	-4.82376	0.206571	-2.37905
C41	-3.88849	1.191008	1.092883
C42	-4.79723	1.164404	2.19951
C43	-4.87765	2.276161	3.07673
C36	-4.09879	3.386787	2.865356
C45	-3.20939	3.416855	1.773408
C46	-3.07997	2.348613	0.899564
H49	-5.57641	2.234145	3.906781
H50	-4.16451	4.244229	3.526712
H51	-2.6052	4.30407	1.613
C48	-0.57515	-0.68541	0.770909
C49	0.094914	-1.49217	1.735722
C50	0.747026	-0.85442	2.821809
C51	0.747474	0.518122	2.923255
C52	0.136183	1.307851	1.923322
C53	-0.51457	0.724209	0.851523
H55	1.252338	-1.46571	3.563459
H56	1.247725	1.005543	3.75359
H57	0.206465	2.390069	1.983438
H53	-6.15563	-1.90595	1.59806
H54	-6.31039	0.004197	3.219919
C55	-0.97749	1.568987	-0.30498
C56	-2.08925	2.465731	-0.2014
C57	-2.12698	3.578349	-1.0528
C58	-1.12267	3.832701	-1.97964
C59	-0.02904	2.965561	-2.09095
C60	0.032548	1.860231	-1.26524
F58	-3.13707	4.454573	-0.99406
F59	-1.20283	4.884821	-2.77095
F60	0.92326	3.214241	-2.9775
F61	1.101237	1.073731	-1.33653
O62	-4.75531	2.155147	-1.76592
C63	-5.33315	3.197376	-2.40203
O64	-5.34613	3.391103	-3.587
C65	-6.06361	4.131269	-1.40911
F66	-5.7827	3.844956	-0.12468

F67	-5.72515	5.400352	-1.64757
F68	-7.38467	3.992589	-1.58925

Table S287.

$[\text{Rh}^{\text{III}}(\text{bisq}^{\text{F4}})(\text{CH}_2\text{TFA}_{\text{eq}}\cdots\text{H}\cdots\text{TFA}_{\text{eq}})(\text{TFA}_{\text{ax}})]^{+\ddagger}$
thermodynamic values

Temp	298.15	498.15
E_{gas}	-3157.75	-3157.75
E_{solv}	-3157.83	-3157.83
G	-3157.46	-3157.54
ZPE	267.137	267.137
H_{vib}	26.952	67.839
S_{trans}	46.135	48.686
S_{rot}	38.778	40.308
S_{vib}	177.206	280.512
solv	-45.6	-45.6

Rh(bisq^{Me2}) complexes

Table S288. Rh^I(bisq^{Me2})(TFA)(TFAH) Cartesian coordinates

Atom	x	y	z
Rh1	-1.16023	0.443504	-1.5711
N2	-1.62523	-0.90382	-0.08568
C3	-1.816	-2.16592	-0.47013
C4	-2.50849	-3.11182	0.308993
C5	-3.04079	-2.71888	1.514207
C6	-5.55928	2.544005	-1.48056
C7	-5.27883	1.33933	-2.0744
C8	-3.97974	0.815751	-1.95064
N9	-2.99599	1.412209	-1.27748
H10	-1.42181	-2.42192	-1.44655
H11	-2.63676	-4.12016	-0.07016
H12	-3.62392	-3.40438	2.12283
H13	-3.71482	-0.11826	-2.43163
O14	0.518685	-0.8032	-1.9271
C15	1.735196	-0.5835	-2.0086
O16	2.351905	0.501432	-2.27398

C17	2.694938	-1.76665	-1.75827
F18	3.434641	-2.01854	-2.85249
F19	3.533498	-1.46866	-0.74496
F20	2.030912	-2.88435	-1.43404
O21	-0.94837	1.843161	-3.15598
C22	0.028866	2.546724	-3.48264
O23	1.255255	2.421789	-3.21127
C24	-0.29106	3.811845	-4.31438
F25	-0.18394	4.903135	-3.51794
F26	0.569601	3.962636	-5.33467
F27	-1.53415	3.792641	-4.81651
H28	1.723356	1.373159	-2.64518
C29	-3.25097	2.611129	-0.63993
C30	-4.54989	3.214707	-0.75019
C31	-4.81221	4.470475	-0.14566
C32	-3.82403	5.121212	0.548363
C33	-2.55418	4.522774	0.676189
C34	-2.24194	3.291033	0.119012
H35	-5.804	4.901894	-0.25105
H36	-4.01275	6.086732	1.008402
H37	-1.78345	5.033632	1.245482
C38	-2.0249	-0.51716	1.178637
C39	-2.80701	-1.40339	1.986634
C40	-3.30329	-0.95672	3.238259
C41	-3.00056	0.304138	3.692044
C42	-2.14929	1.139646	2.935801
C43	-1.64315	0.756534	1.704867
H44	-3.9124	-1.63413	3.830956
H45	-3.37843	0.649619	4.64997
H46	-1.84919	2.101159	3.341798
H47	-6.02148	0.792346	-2.64505
H48	-6.54251	2.999848	-1.56183
C49	-0.85895	2.783755	0.347439
C50	-0.58595	1.608581	1.069862
C51	0.750318	1.280111	1.336222
C52	1.823659	2.042979	0.869665
C53	1.550365	3.214517	0.134587
C54	0.218262	3.566795	-0.09218
H55	0.957308	0.384569	1.917617
H56	0.005221	4.458207	-0.67662

C57	2.665281	4.060851	-0.43021
H58	2.270042	4.936695	-0.95078
H59	3.350321	4.410077	0.352307
H60	3.262202	3.490905	-1.15154
C61	3.241368	1.587738	1.120769
H62	3.703827	1.23326	0.191499
H63	3.871245	2.395803	1.509679
H64	3.269497	0.762683	1.838042

Table S289. Rh^I(bisq^{Me2})(TFA)(TFAH)
thermodynamic values

Temp	298.15	498.15
E_{gas}	-2274.27	-2274.27
E_{solv}	-2274.29	-2274.29
G	-2273.89	-2273.96
ZPE	286.048	286.048
H_{vib}	21.647	56.179
S_{trans}	45.476	48.026
S_{rot}	37.819	39.349
S_{vib}	146.055	234.157
solv	-12.3	-12.3

Table S290. Rh^I(bisq^{Me2})(κ¹-TFA) Cartesian
coordinates

Atom	x	y	z
Rh1	-0.75562	0.719343	-1.98281
N2	-2.55219	-0.57776	0.449075
C3	-3.56258	-1.38281	0.194555
C4	-4.33377	-2.02282	1.194472
C5	-4.00597	-1.80201	2.509807
C6	-5.09139	2.716949	-2.52012
C7	-4.5327	1.998004	-3.55394
C8	-3.24385	1.447445	-3.40496
N9	-2.53161	1.60304	-2.2916
H10	-3.79074	-1.54886	-0.85787
H11	-5.15668	-2.67353	0.914971
H12	-4.56325	-2.27549	3.314767
H13	-2.77678	0.858742	-4.18788

O14	0.966904	-0.61248	-2.00666
C15	0.43316	-1.25402	-2.95404
O16	-0.67629	-0.92491	-3.46413
C17	1.136223	-2.5015	-3.51496
F18	0.380972	-3.59647	-3.29552
F19	1.31472	-2.38227	-4.84498
F20	2.334148	-2.69938	-2.9475
C21	-4.35955	2.897399	-1.31857
C22	-3.05829	2.327734	-1.24474
C23	-2.25411	2.455054	-0.08326
C24	-2.77686	3.138829	0.999324
C25	-4.07581	3.69779	0.94928
C26	-4.85239	3.590199	-0.1829
H27	-2.18114	3.25013	1.899701
H28	-4.45797	4.225442	1.818562
H29	-5.84731	4.024472	-0.21959
C30	-2.91886	-0.94881	2.831154
C31	-2.21106	-0.33736	1.74537
C32	-1.09767	0.527475	2.027987
C33	-0.74868	0.727576	3.356938
C34	-1.44945	0.121054	4.422413
C35	-2.5219	-0.70052	4.169271
H36	0.082611	1.388969	3.58249
H37	-1.13863	0.317597	5.444646
H38	-3.07451	-1.16789	4.980596
H39	-5.06708	1.839672	-4.4847
H40	-6.08679	3.143593	-2.6093
C41	-0.86208	1.9099	-0.13934
C42	-0.28498	1.171561	0.962269
C43	1.093662	1.086922	1.036044
C44	1.977808	1.723632	0.123602
C45	1.456093	2.475773	-0.91716
C46	0.035356	2.549945	-1.07265
H47	1.530166	0.480723	1.825351
H48	-0.35334	3.353674	-1.69402
C49	2.342449	3.195613	-1.90214
H50	1.754788	3.821144	-2.57955
H51	3.078279	3.835066	-1.39982
H52	2.905833	2.482636	-2.51682
C53	3.468116	1.552323	0.299524

H54	3.986506	2.516593	0.368751
H55	3.697506	0.984123	1.205161
H56	3.906232	1.013905	-0.5498

Table S291. Rh^I(bisq^{Me2})(κ¹-TFA) thermodynamic values

Temp	298.15	498.15
E_{gas}	-1747.48	-1747.48
E_{solv}	-1747.50	-1747.50
G	-1747.12	-1747.18
ZPE	262.126	262.126
H_{vib}	17.511	46.524
S_{trans}	44.938	47.488
S_{rot}	37.050	38.581
S_{vib}	112.793	185.891
solv	-10.9	-10.9

Table S292. Rh^I(bisq^{Me2})(κ²-TFA) Cartesian coordinates

Atom	x	y	z
Rh1	-1.41605	0.492084	-2.02229
N2	-2.17792	-0.68795	-0.50895
C3	-2.92894	-1.72177	-0.88939
C4	-3.65095	-2.53283	0.005675
C5	-3.58894	-2.25484	1.348984
C6	-5.51574	3.079554	-1.5692
C7	-5.35835	2.073967	-2.4906
C8	-4.11416	1.42306	-2.57764
N9	-3.06528	1.723512	-1.81078
H10	-2.95827	-1.90748	-1.95651
H11	-4.2444	-3.35389	-0.38217
H12	-4.13982	-2.84689	2.074938
H13	-3.95275	0.626454	-3.29405
O14	-0.289	1.324598	-3.69331
C15	0.552597	0.398575	-3.5253
O16	0.382793	-0.53299	-2.68965
C17	1.828769	0.396638	-4.38292
F18	2.855764	-0.18441	-3.73351

F19	1.629692	-0.28372	-5.53061
F20	2.203001	1.649324	-4.70762
C21	-4.42274	3.452768	-0.74984
C22	-3.17695	2.755314	-0.89614
C23	-2.05431	3.169968	-0.10944
C24	-2.22519	4.218544	0.781179
C25	-3.45839	4.884094	0.945731
C26	-4.54051	4.508486	0.189476
H27	-1.36729	4.537952	1.365481
H28	-3.53982	5.696371	1.662204
H29	-5.49687	5.015483	0.286195
C30	-2.77941	-1.18512	1.804041
C31	-2.05327	-0.40911	0.840131
C32	-1.17906	0.62715	1.299149
C33	-1.09627	0.863458	2.662479
C34	-1.83996	0.125786	3.607913
C35	-2.66474	-0.88734	3.185709
H36	-0.42113	1.641006	3.007317
H37	-1.74341	0.355083	4.665195
H38	-3.2316	-1.48299	3.896364
H39	-6.16489	1.768171	-3.1484
H40	-6.46068	3.605424	-1.4618
C41	-0.67466	2.603255	-0.24079
C42	-0.26899	1.417736	0.408965
C43	1.08189	1.052125	0.355164
C44	2.02979	1.778098	-0.3725
C45	1.624875	2.961232	-1.02099
C46	0.289977	3.363269	-0.91351
H47	1.394219	0.145903	0.867725
H48	-0.02388	4.280521	-1.40515
C49	2.595787	3.777341	-1.84141
H50	2.142102	4.717738	-2.16613
H51	3.50865	4.017442	-1.28352
H52	2.900768	3.231252	-2.74183
C53	3.450863	1.276151	-0.47341
H54	4.18233	2.047264	-0.20396
H55	3.611129	0.41571	0.181937
H56	3.679052	0.957086	-1.49731

Table S293. Rh^I(bisq^{Me2})(κ²-TFA) thermodynamic values

Temp	298.15	498.15
E _{gas}	-1747.48	-1747.48
E _{solv}	-1747.50	-1747.50
G	-1747.12	-1747.18
ZPE	262.442	262.442
H _{vib}	17.369	46.398
S _{trans}	44.938	47.488
S _{rot}	36.875	38.405
S _{vib}	110.741	183.883
solv	-13.7	-13.7

Table S294. Rh^I(bisq^{Me2})(Me) Cartesian coordinates

Atom	x	y	z
Rh1	-1.0902	0.800165	-1.83201
N2	-2.34419	-0.26791	-0.34154
C3	-3.41026	-0.99949	-0.63682
C4	-4.1133	-1.76374	0.31784
C5	-3.67727	-1.7633	1.622815
C6	-5.49695	2.985083	-2.10487
C7	-5.12779	2.299774	-3.23754
C8	-3.81357	1.787405	-3.32739
N9	-2.90174	1.946192	-2.37828
H10	-3.7265	-0.98219	-1.67647
H11	-4.97947	-2.34061	0.009688
H12	-4.18641	-2.34817	2.384779
H13	-3.49768	1.22887	-4.20411
C14	-4.55233	3.185002	-1.0643
C15	-3.23304	2.670519	-1.24746
C16	-2.24095	2.872089	-0.23495
C17	-2.61055	3.529416	0.925125
C18	-3.92747	4.005366	1.125919
C19	-4.87868	3.852571	0.145174
H20	-1.86095	3.693264	1.693956
H21	-4.17762	4.509557	2.055358
H22	-5.88878	4.230891	0.281239

C23	-2.54295	-0.99236	1.982499
C24	-1.90325	-0.23151	0.956936
C25	-0.7579	0.567795	1.246609
C26	-0.27583	0.550879	2.548188
C27	-0.8918	-0.21332	3.565118
C28	-2.01175	-0.96591	3.297443
H29	0.591421	1.15734	2.790975
H30	-0.4773	-0.19304	4.569368
H31	-2.49446	-1.55165	4.075461
H32	-5.82345	2.137245	-4.05488
H33	-6.50452	3.375496	-1.98849
C34	-0.80219	2.480006	-0.4881
C35	-0.09576	1.4014	0.198654
C36	1.330638	1.439795	0.204017
C37	2.075121	2.459092	-0.35817
C38	1.385801	3.568063	-0.93829
C39	0.008126	3.56408	-0.9783
H40	1.848509	0.614932	0.689418
H41	-0.50821	4.416873	-1.4125
C42	0.127221	1.472086	-3.32958
H43	1.132762	1.718901	-2.96816
H44	0.192437	0.616797	-4.02759
H45	-0.26636	2.33637	-3.87954
C46	2.156349	4.741888	-1.49651
H47	1.479122	5.510551	-1.87949
H48	2.797236	5.207833	-0.73685
H49	2.814882	4.438285	-2.32001
C50	3.584587	2.408823	-0.33353
H51	4.018375	3.267432	0.196039
H52	3.937328	1.500601	0.16434
H53	4.011462	2.417239	-1.34489

Table S295. Rh^I(bisq^{Me2})(Me) thermodynamic values

Temp	298.15	498.15
E _{gas}	-1261.14	-1261.14
E _{solv}	-1261.16	-1261.16
G	-1260.77	-1260.82
ZPE	265.844	265.844

H_{vib}	14.479	40.090
S_{trans}	44.382	46.932
S_{rot}	35.779	37.309
S_{vib}	90.221	154.670
solv	-8.9	-8.9

Table S296. Rh^I(bisq^{Me2})(Me)(TFAH) Cartesian coordinates

Atom	x	y	z
Rh1	-1.38751	0.54118	-2.32016
N2	-2.22465	-0.20368	-0.24147
C3	-3.25101	-0.98254	-0.56232
C4	-3.93418	-1.81574	0.34644
C5	-3.50902	-1.84275	1.650347
C6	-5.13608	3.463787	-2.09207
C7	-4.70439	2.921196	-3.27793
C8	-3.44793	2.289774	-3.32691
N9	-2.6204	2.196378	-2.2784
H10	-3.54301	-0.96129	-1.60894
H11	-4.76394	-2.42298	7.5E-05
H12	-3.98802	-2.48062	2.389095
H13	-3.10781	1.815636	-4.23783
O14	-0.37208	-1.36947	-2.4493
C15	0.85184	-1.26408	-2.4188
O16	1.500137	-0.14153	-2.27349
C17	1.762181	-2.49181	-2.55146
F18	2.535344	-2.37858	-3.6449
F19	2.56437	-2.59282	-1.47608
F20	1.041683	-3.61196	-2.6511
H21	0.750037	0.571247	-2.2233
C22	-4.27133	3.445589	-0.96929
C23	-2.97416	2.853142	-1.10915
C24	-2.05487	2.945072	-0.02031
C25	-2.48495	3.504764	1.173088
C26	-3.79037	4.013211	1.336057
C27	-4.6611	4.006726	0.273549
H28	-1.77833	3.579335	1.994191
H29	-4.08662	4.439294	2.290379
H30	-5.65642	4.434486	0.362268

C31	-2.42185	-1.02732	2.048631
C32	-1.79845	-0.1829	1.066528
C33	-0.71088	0.659174	1.48386
C34	-0.29024	0.586572	2.805332
C35	-0.89355	-0.2605	3.756631
C36	-1.95265	-1.05048	3.386267
H37	0.52798	1.228794	3.117199
H38	-0.52397	-0.27138	4.777964
H39	-2.44575	-1.70306	4.102099
H40	-5.32072	2.93821	-4.17103
H41	-6.11892	3.917839	-1.99906
C42	-0.60256	2.615945	-0.14973
C43	0.023901	1.599353	0.592972
C44	1.425463	1.512174	0.553028
C45	2.220397	2.383608	-0.19177
C46	1.589125	3.404333	-0.9335
C47	0.198374	3.500035	-0.88828
H48	1.909185	0.7132	1.109216
H51	-0.29097	4.295817	-1.4438
C52	-0.81828	0.920955	-4.26509
H53	-0.81834	1.994764	-4.49709
H54	0.177368	0.533302	-4.52486
H55	-1.53389	0.418758	-4.93727
C55	2.394136	4.379479	-1.7596
H56	1.745545	5.106912	-2.25506
H57	3.115094	4.934366	-1.14605
H58	2.97206	3.864561	-2.53696
C58	3.721641	2.219667	-0.21023
H59	4.23528	3.131794	0.118438
H60	4.037864	1.402916	0.444324
H61	4.087498	1.995603	-1.21977

Table S297. Rh^I(bisq^{Me2})(Me)(TFAH) thermodynamic values

Temp	298.15	498.15
E_{gas}	-1787.93	-1787.93
E_{solv}	-1787.94	-1787.94
G	-1787.52	-1787.59
ZPE	291.522	291.522

H_{vib}	19.162	50.576
S_{trans}	45.019	47.569
S_{rot}	37.117	38.647
S_{vib}	123.832	202.998
solv	-9.1	-9.1

Table S298. Rh^{II}(bisq^{Me2})(TFA)₂ Cartesian coordinates

Atom	x	y	z
Rh1	-0.88649	0.764223	-1.93344
N2	-1.60717	-0.7285	-0.63016
C3	-2.06614	-1.86039	-1.15368
C4	-2.8519	-2.77148	-0.41674
C5	-3.18042	-2.47358	0.88364
C6	-5.22785	3.006909	-1.62804
C7	-5.01384	1.913526	-2.43048
C8	-3.73396	1.327346	-2.44903
N9	-2.72271	1.767317	-1.70672
H10	-1.77732	-2.04928	-2.18366
H11	-3.1956	-3.68074	-0.89781
H12	-3.81	-3.13769	1.469597
H13	-3.50756	0.500466	-3.1128
O14	0.960006	-0.11113	-2.18716
C15	1.06704	-1.26676	-2.7376
O16	0.198389	-2.02377	-3.15887
C17	2.553138	-1.71272	-2.78762
F18	2.984386	-2.00773	-1.53462
F19	2.730029	-2.80222	-3.54611
F20	3.358297	-0.73892	-3.26495
O21	-0.30963	2.186743	-3.35459
C22	-0.83185	1.762388	-4.44349
O23	-1.55983	0.769865	-4.57009
C24	-0.49121	2.631016	-5.67541
F25	-0.94548	3.892689	-5.4985
F26	0.840326	2.697462	-5.86572
F27	-1.04822	2.148907	-6.79505
C29	-4.1697	3.518728	-0.83792
C30	-2.89982	2.85741	-0.8826
C31	-1.81909	3.363724	-0.09343

C32	-2.03586	4.505251	0.661634
C33	-3.28453	5.162048	0.699939
C34	-4.33869	4.671383	-0.03007
H35	-1.2107	4.897506	1.248902
H36	-3.40368	6.051197	1.311704
H37	-5.30933	5.159045	-0.01231
C38	-2.68138	-1.28914	1.482019
C39	-1.84736	-0.43801	0.693707
C40	-1.25041	0.714881	1.284126
C41	-1.56104	1.018924	2.597791
C42	-2.43331	0.213264	3.363895
C43	-2.97075	-0.93059	2.823086
H44	-1.09829	1.888508	3.055168
H45	-2.65324	0.490159	4.390615
H46	-3.61484	-1.5782	3.411739
H47	-5.79516	1.502443	-3.06018
H48	-6.19613	3.499217	-1.59596
C49	-0.45765	2.747823	-0.0649
C50	-0.20105	1.505034	0.561271
C51	1.128105	1.052476	0.638714
C52	2.193147	1.752652	0.080733
C53	1.939464	3.004351	-0.5258
C54	0.631627	3.482307	-0.5662
H55	1.31984	0.095865	1.116971
H56	0.431361	4.432457	-1.0527
C57	3.053295	3.793134	-1.16848
H58	2.686616	4.74109	-1.57013
H59	3.860733	4.012819	-0.45956
H60	3.49889	3.229872	-1.99685
C61	3.569806	1.137233	0.064127
H62	4.348165	1.846726	0.364467
H63	3.622588	0.269215	0.726464
H64	3.810388	0.788458	-0.94743

Table S299. Rh^{II}(bisq^{Me2})(TFA)₂ thermodynamic values

Temp	298.15	498.15
E_{gas}	-2273.67	-2273.67
E_{solv}	-2273.70	-2273.70

G	-2273.30	-2273.37
ZPE	281.052	281.052
H_{vib}	21.482	55.643
S_{trans}	45.471	48.021
S_{rot}	37.778	39.308
S_{vib}	144.492	231.670
solv	-19.1	-19.1

Table S300. $[\text{Rh}^{\text{II}}(\text{bisq}^{\text{Me2}})(\text{TFA})(\text{TFAH})]^+$
Cartesian coordinates

Atom	x	y	z
Rh1	-1.1595	0.560648	-1.48637
N2	-1.80936	-0.87024	-0.14186
C3	-2.1374	-2.08372	-0.57145
C4	-2.7882	-3.02663	0.246095
C5	-3.12639	-2.66911	1.531926
C6	-5.58952	2.539465	-1.59142
C7	-5.25757	1.394791	-2.27694
C8	-3.95203	0.895245	-2.14855
N9	-3.01962	1.467693	-1.39133
H10	-1.8859	-2.31621	-1.60191
H11	-3.02778	-4.00422	-0.15681
H12	-3.6593	-3.35984	2.179207
H13	-3.65374	0.001698	-2.68854
O14	0.514456	-0.72924	-1.70559
C15	1.745933	-0.63882	-1.85714
O16	2.436868	0.360263	-2.23243
C17	2.581864	-1.88398	-1.47826
F18	3.700862	-1.96363	-2.19473
F19	2.90666	-1.7771	-0.1715
F20	1.868413	-3.00174	-1.64752
O21	-0.83903	1.948826	-3.01437
C22	0.194222	2.563065	-3.39912
O23	1.396045	2.349673	-3.13283
C24	-0.09801	3.808231	-4.27465
F25	-0.31159	4.858834	-3.44719
F26	0.928733	4.101374	-5.07243
F27	-1.19474	3.635723	-5.02218
H28	1.872834	1.238868	-2.57504

C29	-3.30978	2.618027	-0.69059
C30	-4.62285	3.185561	-0.78507
C31	-4.9217	4.38911	-0.0964
C32	-3.95232	5.01956	0.644184
C33	-2.65877	4.46258	0.728323
C34	-2.31674	3.278061	0.094402
H35	-5.922	4.803832	-0.17875
H36	-4.17117	5.946086	1.165319
H37	-1.90115	4.972327	1.316006
C38	-2.05162	-0.51012	1.162439
C39	-2.76661	-1.39199	2.029027
C40	-3.07011	-0.96371	3.346567
C41	-2.65687	0.273912	3.78147
C42	-1.88938	1.108562	2.936688
C43	-1.56987	0.737803	1.642068
H44	-3.62141	-1.6304	4.003092
H45	-2.88656	0.604042	4.789595
H46	-1.51116	2.050481	3.3228
H47	-5.96701	0.879227	-2.91393
H48	-6.5854	2.967001	-1.6667
C49	-0.91518	2.789438	0.227522
C50	-0.58613	1.559585	0.855075
C51	0.78409	1.242531	1.026128
C52	1.812922	2.082682	0.613987
C53	1.47536	3.319161	0.002148
C54	0.130142	3.637404	-0.17934
H55	1.03481	0.312888	1.530373
H56	-0.12543	4.568278	-0.6771
C57	2.548264	4.263825	-0.47225
H58	2.122409	5.206168	-0.82367
H59	3.267721	4.487464	0.322955
H60	3.111582	3.823092	-1.30332
C61	3.254048	1.687914	0.826701
H62	3.815963	1.717672	-0.11301
H63	3.756223	2.370705	1.52239
H64	3.333325	0.675431	1.229244

Table S301. $[\text{Rh}^{\text{II}}(\text{bisq}^{\text{Me2}})(\text{TFA})(\text{TFAH})]^+$
thermodynamic values

Temp	298.15	498.15
E _{gas}	-2274.06	-2274.06
E _{solv}	-2274.13	-2274.13
G	-2273.72	-2273.79
ZPE	287.900	287.900
H _{vib}	21.379	55.677
S _{trans}	45.476	48.026
S _{rot}	37.779	39.309
S _{vib}	143.230	230.733
solv	-40.3	-40.3

Table S302. Rh^{III}(bisq^{Me2})(Me_{ax})(H_{eq})(TFA_{eq})
Cartesian coordinates

Atom	x	y	z
Rh1	-1.61447	0.168669	-1.98882
N2	-2.28816	-0.99171	0.160609
C3	-3.03038	-2.05996	-0.07522
C4	-3.47498	-2.95635	0.920809
C5	-3.10703	-2.72222	2.220997
C6	-6.20072	1.798429	-1.87531
C7	-5.72519	1.192921	-3.0134
C8	-4.37235	0.801474	-3.06602
N9	-3.51409	1.020932	-2.07599
H10	-3.28834	-2.2422	-1.1131
H11	-4.08216	-3.8115	0.642207
H12	-3.41164	-3.38947	3.023105
H13	-3.98159	0.268098	-3.92388
O14	0.220126	-0.71725	-1.75742
C15	1.27551	-0.35754	-2.39624
O16	1.440948	0.488994	-3.26615
C17	2.508163	-1.15506	-1.88504
F18	3.621495	-0.85165	-2.57298
F19	2.753417	-0.86501	-0.58019
F20	2.321882	-2.48823	-1.97215
H21	-1.21179	0.823491	-3.30149
C22	-3.93398	1.729434	-0.96809
C23	-5.30981	2.081998	-0.80986
C24	-5.73617	2.698213	0.393793
C25	-4.82478	2.975497	1.384929

C26	-3.45408	2.697871	1.189336
C27	-2.98367	2.101139	0.031236
H28	-6.78741	2.946234	0.512844
H29	-5.14759	3.44206	2.31104
H30	-2.74044	2.986142	1.954259
C31	-1.91921	-0.72475	1.455813
C32	-2.30708	-1.5942	2.528399
C33	-1.88406	-1.32863	3.855385
C34	-1.0903	-0.23961	4.120262
C35	-0.7091	0.623841	3.07149
C36	-1.10861	0.419481	1.759959
H37	-2.19352	-2.00417	4.648689
H38	-0.7567	-0.03382	5.133185
H39	-0.08829	1.487087	3.293719
H40	-6.37121	0.97949	-3.85835
H41	-7.24804	2.072137	-1.77883
C42	-1.50966	1.986446	-0.20356
C43	-0.62966	1.343624	0.703129
C44	0.745628	1.545431	0.563456
C45	1.30066	2.33402	-0.45138
C46	0.440764	2.942804	-1.38177
C47	-0.9414	2.760384	-1.23794
H48	1.414361	1.012787	1.233217
H49	-1.60781	3.284307	-1.91687
C50	-2.0964	-1.41308	-3.20388
H51	-1.85944	-1.20645	-4.25153
H52	-1.49297	-2.25861	-2.86208
H53	-3.1637	-1.6565	-3.12167
C54	2.798945	2.44495	-0.5903
H55	3.130206	3.490135	-0.60543
H56	3.312031	1.935429	0.228784
H57	3.126347	1.985971	-1.53035
C58	0.978581	3.721809	-2.55364
H59	0.176995	4.239659	-3.08768
H60	1.722545	4.46633	-2.24872
H61	1.460199	3.028545	-3.25294

Table S303. Rh^{III}(bisq^{Me2})(Me_{ax})(H_{eq})(TFA_{eq})
thermodynamic values

Temp	298.15	498.15
E _{gas}	-1787.96	-1787.96
E _{solv}	-1787.99	-1787.99
G	-1787.56	-1787.63
ZPE	291.587	291.587
H _{vib}	18.873	50.281
S _{trans}	45.019	47.569
S _{rot}	36.966	38.496
S _{vib}	120.574	199.716
solv	-14.4	-14.4

Table S304. Rh^{III}(bisq^{Me2})(Me_{eq})(H_{ax})(TFA_{eq})
Cartesian coordinates

Atom	x	y	z
Rh1	-1.54511	0.270444	-1.79516
N2	-1.49591	-1.27388	-0.05291
C3	-1.58947	-2.55804	-0.36462
C4	-2.08177	-3.53237	0.535343
C5	-2.50997	-3.13817	1.780239
C6	-6.25316	1.264964	-0.93184
C7	-5.86272	0.120907	-1.58271
C8	-4.4887	-0.12092	-1.7656
N9	-3.5314	0.685822	-1.31296
H10	-1.2525	-2.81875	-1.36482
H11	-2.12994	-4.57002	0.221197
H12	-2.92345	-3.85438	2.486314
H13	-1.94458	-0.78629	-2.80373
H14	-4.14964	-0.99248	-2.31156
O15	0.428221	0.006496	-2.28985
C16	0.913622	-1.1269	-2.64226
O17	0.37703	-2.22036	-2.79359
C18	2.452779	-1.03337	-2.83206
F19	2.93019	-2.02672	-3.59579
F20	2.842198	0.135449	-3.38869
F21	3.065909	-1.11635	-1.62168
C22	-3.88751	1.822365	-0.61205
C23	-5.27021	2.155415	-0.43561
C24	-5.63067	3.362671	0.215157
C25	-4.65844	4.214736	0.677532

C26	-3.29773	3.869288	0.535824
C27	-2.88751	2.694168	-0.07445
H28	-6.68519	3.597436	0.33209
H29	-4.92782	5.145677	1.167568
H30	-2.5367	4.533244	0.935421
C31	-1.83765	-0.86766	1.210692
C32	-2.39617	-1.77621	2.161041
C33	-2.79728	-1.29309	3.432842
C34	-2.62503	0.032916	3.754432
C35	-2.0168	0.916988	2.832909
C36	-1.61604	0.492787	1.579477
H37	-3.23209	-1.98822	4.146237
H38	-2.93045	0.403762	4.728626
H39	-1.8372	1.948335	3.122737
H40	-6.58283	-0.58756	-1.97789
H41	-7.30382	1.505282	-0.79281
C42	-1.41921	2.407945	-0.11373
C43	-0.83342	1.397096	0.678527
C44	0.567552	1.292961	0.714344
C45	1.404459	2.129861	-0.01766
C46	0.821726	3.156347	-0.79625
C47	-0.56414	3.284001	-0.81251
H48	1.009165	0.508844	1.323559
H49	-1.01343	4.067823	-1.4162
C50	-1.7211	1.527858	-3.42112
H51	-2.30494	1.073883	-4.22836
H52	-2.20618	2.465805	-3.12597
H53	-0.70868	1.73099	-3.78026
C54	2.895695	1.904785	-0.01351
H55	3.451782	2.827948	0.185891
H56	3.180521	1.165603	0.739657
H57	3.225903	1.524399	-0.98688
C58	1.681176	4.072389	-1.63277
H59	1.075349	4.815113	-2.15877
H60	2.420505	4.607689	-1.02444
H61	2.239331	3.500985	-2.38417

Table S305. Rh^{III}(bisq^{Me2})(Me_{eq})(H_{ax})(TFA_{eq})
thermodynamic values

Temp	298.15	498.15
E _{gas}	-1787.96	-1787.96
E _{solv}	-1787.99	-1787.99
G	-1787.57	-1787.63
ZPE	291.359	291.359
H _{vib}	19.087	50.497
S _{trans}	45.019	47.569
S _{rot}	36.987	38.517
S _{vib}	123.404	202.550
solv	-14.7	-14.7

Table S306. Rh^{III}(bisq^{Me2})(Me_{eq})(H_{eq})(TFA_{ax})
Cartesian coordinates

Atom	x	y	z
Rh1	-1.48837	0.298915	-1.99415
N2	-2.26996	-1.07574	-0.37969
C3	-2.99438	-2.15273	-0.63134
C4	-3.43633	-3.03027	0.385018
C5	-3.09792	-2.76645	1.690534
C6	-6.3275	1.735778	-1.60847
C7	-5.93491	0.991286	-2.69529
C8	-4.56005	0.70854	-2.87545
N9	-3.6268	1.1584	-2.05563
H10	-3.21765	-2.33714	-1.67815
H11	-4.02784	-3.89975	0.117751
H12	-3.41472	-3.42343	2.496558
O13	-2.18545	-1.05717	-3.34132
H14	-4.20881	0.070592	-3.68232
H15	-0.09847	-0.35122	-1.99904
C16	-1.47951	-1.8747	-4.05774
O17	-0.27811	-2.03485	-4.14675
C18	-2.44355	-2.78152	-4.87408
F19	-1.7904	-3.59553	-5.71002
F20	-3.18052	-3.55988	-4.0361
F21	-3.31819	-2.05143	-5.60468
C22	-3.98403	1.931157	-0.98609
C23	-5.35137	2.229742	-0.70449
C24	-5.66994	2.995199	0.445553
C25	-4.66674	3.452549	1.268295

C26	-3.31156	3.183878	0.96406
C27	-2.9529	2.435799	-0.14321
H28	-6.71205	3.215125	0.661981
H29	-4.90808	4.03799	2.150659
H30	-2.53227	3.583482	1.60677
C31	-1.91606	-0.7876	0.908366
C32	-2.31083	-1.62628	1.994679
C33	-1.88777	-1.30464	3.308827
C34	-1.09357	-0.20284	3.524601
C35	-0.7019	0.619665	2.443569
C36	-1.10507	0.357195	1.144765
H37	-2.18931	-1.94599	4.132721
H38	-0.75931	0.042564	4.528447
H39	-0.07148	1.483694	2.634178
H40	-6.65759	0.601108	-3.40449
H41	-7.37722	1.952785	-1.42695
C42	-1.49898	2.283008	-0.50392
C43	-0.65049	1.275564	0.044723
C44	0.760498	1.450309	-0.09841
C45	1.331112	2.544945	-0.71539
C46	0.478752	3.564229	-1.23105
C47	-0.89059	3.409797	-1.11925
H48	1.402852	0.682227	0.323023
H49	-1.54308	4.189926	-1.50171
C50	-0.71712	1.394571	-3.56466
H51	-0.49821	0.710749	-4.3869
H52	-1.45983	2.135655	-3.88239
H53	0.203849	1.904551	-3.27011
C54	2.831475	2.654991	-0.83994
H55	3.212366	3.578367	-0.38695
H56	3.329667	1.811173	-0.35576
H57	3.142725	2.665046	-1.8916
C58	1.057167	4.793562	-1.88842
H59	0.267809	5.478888	-2.2077
H60	1.725234	5.33893	-1.21045
H61	1.649678	4.53078	-2.77287

Table S307. Rh^{III}(bisq^{Me2})(Me_{eq})(H_{eq})(TFA_{ax})
thermodynamic values

Temp	298.15	498.15
E _{gas}	-1787.95	-1787.95
E _{solv}	-1787.97	-1787.97
G	-1787.55	-1787.62
ZPE	291.233	291.233
H _{vib}	19.037	50.465
S _{trans}	45.019	47.569
S _{rot}	37.135	38.665
S _{vib}	122.372	201.567
solv	-14.9	-14.9

Table S308. Rh^{III}(bisq^{Me2})(TFA)₃ Cartesian coordinates

Atom	x	y	z
Rh1	-1.63378	0.344652	-1.77592
N2	-2.36148	-0.84371	-0.20704
C3	-3.09572	-1.92149	-0.44146
C4	-3.47106	-2.81421	0.58254
C5	-3.03737	-2.58081	1.864981
C6	-6.33484	1.656454	-1.77943
C7	-5.77848	1.073588	-2.89178
C8	-4.3846	0.849526	-2.93692
N9	-3.577	1.224887	-1.95256
H10	-3.35524	-2.10012	-1.47915
H11	-4.07411	-3.68015	0.332882
H12	-3.28873	-3.26129	2.674112
O13	-2.32188	-1.06254	-3.04192
H14	-3.91428	0.343491	-3.7694
O15	-0.00765	-0.8571	-1.49827
C16	1.184524	-0.74545	-2.00444
O17	1.798507	0.221712	-2.40624
C18	1.88937	-2.13305	-1.9441
F19	3.033105	-2.13398	-2.63904
F20	2.193602	-2.43052	-0.65344
F21	1.113404	-3.12701	-2.41306
O22	-0.75531	1.556753	-3.14697
C23	-1.18407	1.755528	-4.34572
O24	-2.17417	1.324662	-4.9194
C25	-0.28562	2.779943	-5.09479

F26	-0.28334	2.556669	-6.41351
F27	-0.78261	4.030425	-4.8884
F28	0.991606	2.789152	-4.66931
C29	-1.63693	-1.57284	-4.03556
O30	-0.50825	-1.36794	-4.41295
C31	-2.56029	-2.58148	-4.77874
F32	-1.90881	-3.22613	-5.74642
F33	-3.05824	-3.50546	-3.9202
F34	-3.61492	-1.94071	-5.33148
C35	-4.08845	1.912535	-0.87612
C36	-5.49395	2.100087	-0.72694
C37	-5.98172	2.736068	0.443182
C38	-5.10654	3.197036	1.399651
C39	-3.71094	3.083303	1.202704
C40	-3.19352	2.461213	0.081386
H41	-7.05431	2.86269	0.56225
H42	-5.48178	3.6842	2.294517
H43	-3.02915	3.51878	1.927092
C44	-1.91905	-0.56575	1.063399
C45	-2.23375	-1.4473	2.142032
C46	-1.71718	-1.17736	3.434262
C47	-0.91402	-0.08126	3.640035
C48	-0.61843	0.792943	2.570868
C49	-1.11324	0.583868	1.294581
H50	-1.95609	-1.85705	4.247322
H51	-0.50476	0.122792	4.624777
H52	0.008757	1.661265	2.750856
H53	-6.38601	0.748353	-3.72911
H54	-7.40944	1.797304	-1.69719
C55	-1.73503	2.521123	-0.24376
C56	-0.77737	1.577091	0.222954
C57	0.590141	1.830127	-0.06153
C58	1.015639	2.921195	-0.8013
C59	0.052452	3.866224	-1.24441
C60	-1.28874	3.648711	-0.95343
H61	1.324312	1.11608	0.295541
H64	-2.02831	4.365798	-1.29846
C64	0.467263	5.074255	-2.04313
H65	-0.39031	5.709888	-2.27626
H66	1.206223	5.677761	-1.50305

H67	0.924763	4.768121	-2.98901
C67	2.46519	3.064153	-1.17904
H68	2.845958	4.072324	-0.98335
H69	3.087296	2.343421	-0.64491
H70	2.576705	2.856875	-2.24903

Table S309. $\text{Rh}^{\text{III}}(\text{bisq}^{\text{Me}_2})(\text{TFA})_3$ thermodynamic values

Temp	298.15	498.15
E_{gas}	-2799.82	-2799.82
E_{solv}	-2799.86	-2799.86
G	-2799.44	-2799.52
ZPE	299.754	299.754
H_{vib}	26.206	66.367
S_{trans}	45.924	48.474
S_{rot}	38.386	39.916
S_{vib}	172.777	274.180
solv	-22.0	-22.0

Table S310. $[\text{Rh}^{\text{III}}(\text{bisq}^{\text{Me}_2})(\text{TFA})_2(\text{TFAH}_{\text{eq}})]^+$ Cartesian coordinates

Atom	x	y	z
Rh1	-1.61987	0.426094	-1.91575
N2	-2.24296	-0.84558	-0.36532
C3	-3.06203	-1.83977	-0.70324
C4	-3.48482	-2.8281	0.199874
C5	-3.02644	-2.77985	1.493359
C6	-6.19398	1.917841	-1.77648
C7	-5.73026	1.282019	-2.90599
C8	-4.37494	0.902543	-2.98154
N9	-3.52184	1.178662	-2.00245
H10	-3.38094	-1.86865	-1.73695
H11	-4.14389	-3.61477	-0.14896
H12	-3.30941	-3.53826	2.217613
O13	-2.24866	-0.87469	-3.34908
H14	-3.98397	0.33119	-3.81468
O15	0.283764	-0.42459	-1.54635
C16	1.309785	-0.79134	-2.14297

O17	1.65138	-0.62946	-3.35705
C18	2.383806	-1.46755	-1.2569
F19	3.270792	-2.14577	-1.97401
F20	3.030336	-0.49297	-0.57287
F21	1.805778	-2.28494	-0.37067
O22	-1.22804	1.743309	-3.46597
C23	-0.64302	1.494143	-4.57038
O24	0.129135	0.574529	-4.87262
C25	-0.98231	2.553806	-5.65243
F26	-0.37482	2.296288	-6.80642
F27	-2.31258	2.582829	-5.85739
F28	-0.59671	3.772692	-5.22111
H29	0.922597	-0.15893	-3.95912
C30	-1.65738	-1.97634	-3.74126
O31	-0.60389	-2.46228	-3.39599
C32	-2.59977	-2.70915	-4.73956
F33	-1.99189	-3.73617	-5.32022
F34	-3.67173	-3.17458	-4.04769
F35	-3.05823	-1.87447	-5.68846
C36	-3.92352	1.900346	-0.90323
C37	-5.29418	2.245271	-0.73071
C38	-5.67983	2.902289	0.465969
C39	-4.73617	3.214624	1.418502
C40	-3.36778	2.933036	1.195455
C41	-2.94606	2.292401	0.044053
H42	-6.72487	3.158027	0.613236
H43	-5.0322	3.715563	2.334705
H44	-2.63146	3.256667	1.92539
C45	-1.79665	-0.73217	0.937812
C46	-2.16985	-1.72841	1.896891
C47	-1.67252	-1.65609	3.223442
C48	-0.83592	-0.63344	3.596497
C49	-0.48553	0.358809	2.659018
C50	-0.95187	0.342703	1.352294
H51	-1.96194	-2.42773	3.930319
H52	-0.44819	-0.57615	4.608332
H53	0.155193	1.177975	2.971388
H54	-6.38879	1.036026	-3.73129
H55	-7.24355	2.180238	-1.67763
C56	-1.48617	2.194824	-0.31407

C57	-0.54007	1.442641	0.447245
C58	0.816959	1.77581	0.355354
C59	1.285562	2.814631	-0.45178
C60	0.361519	3.569139	-1.22659
C61	-0.98345	3.260847	-1.1241
H62	1.535989	1.168481	0.894576
H63	-1.70308	3.852611	-1.681
C64	0.823768	4.672241	-2.1451
H65	-0.01947	5.133214	-2.66295
H66	1.361357	5.455449	-1.5989
H67	1.50897	4.288861	-2.90996
C68	2.759546	3.10713	-0.52313
H69	3.127652	3.023671	-1.5527
H70	2.972058	4.133568	-0.20075
H71	3.338009	2.423253	0.100469

Table S311. $[\text{Rh}^{\text{III}}(\text{bisq}^{\text{Me2}})(\text{TFA})_2(\text{TFAH}_{\text{eq}})]^+$
thermodynamic values

Temp	298.15	498.15
E_{gas}	-2800.22	-2800.22
E_{solv}	-2800.29	-2800.29
G	-2799.85	-2799.94
ZPE	307.326	307.326
H_{vib}	25.650	65.491
S_{trans}	45.928	48.478
S_{rot}	38.424	39.954
S_{vib}	173.087	274.660
solv	-42.3	-42.3

Table S312. $[\text{Rh}^{\text{III}}(\text{bisq}^{\text{Me2}})(\kappa^1\text{-TFA}_{\text{ax}})(\kappa^2\text{-TFA}_{\text{eq,eq}})]^+$
Cartesian coordinates

Atom	x	y	z
Rh1	-1.25931	0.471036	-1.94593
N2	-2.04993	-0.89893	-0.6111
C3	-2.63233	-2.03063	-0.99249
C4	-3.27743	-2.88051	-0.07181
C5	-3.34364	-2.51599	1.253456
C6	-5.5074	2.866712	-1.46921

C7	-5.39226	1.715492	-2.20909
C8	-4.13912	1.085252	-2.29885
N9	-3.04768	1.552358	-1.69545
H10	-2.61178	-2.25045	-2.05338
H11	-3.72974	-3.79706	-0.43369
H12	-3.86297	-3.13854	1.976216
H13	-4.00726	0.192905	-2.89814
O14	-0.12235	1.55845	-3.36455
C15	0.70336	0.595195	-3.40047
O16	0.579974	-0.36098	-2.57117
C17	1.902385	0.631079	-4.36007
F18	2.933959	1.234115	-3.70536
F19	2.28557	-0.59577	-4.69498
F20	1.627809	1.342187	-5.44713
C21	-4.36721	3.400628	-0.82267
C22	-3.11965	2.709806	-0.9458
C23	-1.95914	3.256864	-0.32978
C24	-2.06886	4.454597	0.360281
C25	-3.2987	5.131549	0.493096
C26	-4.43074	4.610653	-0.08524
H27	-1.1801	4.872823	0.823298
H28	-3.34133	6.061576	1.050634
H29	-5.38607	5.120274	-0.00184
C30	-2.72311	-1.31749	1.687159
C31	-2.03678	-0.5341	0.714534
C32	-1.32006	0.627271	1.090418
C33	-1.36376	1.029861	2.414014
C34	-2.08991	0.295604	3.380202
C35	-2.74099	-0.86645	3.03149
H36	-0.80482	1.90839	2.722404
H37	-2.10397	0.639914	4.409346
H38	-3.2681	-1.4543	3.777151
H39	-6.23716	1.281674	-2.73194
H40	-6.4584	3.384266	-1.37986
C41	-0.62687	2.605336	-0.41449
C42	-0.39179	1.295	0.109111
C43	0.956316	0.819009	0.113653
C44	2.022649	1.554901	-0.37189
C45	1.767733	2.861512	-0.88491
C46	0.460179	3.345329	-0.90372

H47	1.142979	-0.16261	0.539783
H50	0.268796	4.329094	-1.32069
O51	-2.17897	-0.59395	-3.41733
C52	-1.73588	-0.90998	-4.60941
O53	-0.69842	-0.63022	-5.16782
C54	-2.80432	-1.80609	-5.30144
F55	-2.96123	-2.94864	-4.59213
F56	-3.99954	-1.17784	-5.33099
F57	-2.4528	-2.11831	-6.54143
C57	2.891323	3.708094	-1.41687
H58	2.545558	4.706162	-1.69354
H59	3.694999	3.812165	-0.6794
H60	3.331654	3.241232	-2.305
C60	3.417662	0.982038	-0.35514
H61	4.11333	1.626833	0.193164
H62	3.432547	-0.00577	0.110981
H63	3.804785	0.879186	-1.3743

Table S313. $[\text{Rh}^{\text{III}}(\text{bisq}^{\text{Me}_2})(\kappa^1\text{-TFA}_{\text{ax}})(\kappa^2\text{-TFA}_{\text{eq,eq}})]^+$ thermodynamic values

Temp	298.15	498.15
E_{gas}	-2273.44	-2273.44
E_{solv}	-2273.50	-2273.50
G	-2273.10	-2273.17
ZPE	282.914	282.914
H_{vib}	21.142	55.504
S_{trans}	45.471	48.021
S_{rot}	37.731	39.261
S_{vib}	135.719	222.391
solv	-42.0	-42.0

Table S314. $[\text{Rh}^{\text{III}}(\text{bisq}^{\text{Me}_2})(\kappa^1\text{-TFA}_{\text{eq}})(\kappa^2\text{-TFA}_{\text{ax,eq}})]^+$ Cartesian coordinates

Atom	x	y	z
Rh1	-1.30031	0.669009	-1.95168
N2	-2.34792	-0.40434	-0.46655
C3	-3.339	-1.20109	-0.86033
C4	-4.09086	-1.98494	0.031854

C5	-3.78573	-1.94092	1.371872
C6	-5.43861	3.110608	-2.03023
C7	-5.11984	2.278564	-3.07994
C8	-3.86678	1.632456	-3.09884
N9	-2.97333	1.829198	-2.13615
H10	-3.53202	-1.2372	-1.92627
H11	-4.88327	-2.61569	-0.35464
H12	-4.33413	-2.5436	2.09025
H13	-3.56368	0.975569	-3.906
O14	0.200721	-0.87923	-2.04877
C15	-0.49187	-1.44094	-2.93979
O16	-1.60434	-0.92218	-3.29226
C17	-0.05062	-2.77545	-3.56375
F18	-0.60722	-3.77581	-2.85435
F19	-0.4641	-2.85988	-4.82898
F20	1.27608	-2.89525	-3.51576
O21	-0.18589	1.608005	-3.36905
C22	-0.63348	1.84985	-4.56704
O23	-1.71322	1.583717	-5.06249
C24	0.423424	2.652362	-5.37525
F25	0.1275	2.681954	-6.67252
F26	0.448562	3.926917	-4.91301
F27	1.661107	2.141883	-5.22568
C28	-4.49411	3.342603	-0.99812
C29	-3.23149	2.693435	-1.09924
C30	-2.21036	2.921514	-0.14588
C31	-2.48493	3.750767	0.926438
C32	-3.75157	4.365337	1.069435
C33	-4.73254	4.181497	0.120623
H34	-1.70806	3.954662	1.657583
H35	-3.93568	5.008361	1.924214
H36	-5.69442	4.677355	0.212264
C37	-2.73484	-1.10922	1.82796
C38	-2.02522	-0.32	0.869743
C39	-0.95786	0.517979	1.301498
C40	-0.61172	0.516629	2.643686
C41	-1.30636	-0.26439	3.591942
C42	-2.35533	-1.05756	3.193773
H43	0.207531	1.148271	2.973959
H44	-1.00685	-0.22995	4.634433

H45	-2.89931	-1.66482	3.911158
H46	-5.81432	2.096805	-3.89228
H47	-6.40723	3.599931	-1.9846
C48	-0.82458	2.401551	-0.4238
C49	-0.19319	1.378567	0.360789
C50	1.199706	1.247812	0.301452
C51	2.001634	2.085773	-0.47777
C52	1.398625	3.12659	-1.2405
C53	0.025535	3.270852	-1.17888
H54	1.66758	0.444805	0.862339
H55	-0.44639	4.070446	-1.74194
C56	2.223118	4.020761	-2.1295
H57	1.617678	4.825053	-2.55132
H58	3.066227	4.467482	-1.59258
H59	2.631544	3.447703	-2.97004
C60	3.487812	1.870656	-0.52639
H61	4.028464	2.773583	-0.21887
H62	3.798878	1.045582	0.117305
H63	3.809982	1.647365	-1.55075

Table S315. $[\text{Rh}^{\text{III}}(\text{bisq}^{\text{Me2}})(\kappa^1\text{-TFA}_{\text{eq}})(\kappa^2\text{-TFA}_{\text{ax,eq}})]^+$ thermodynamic values

Temp	298.15	498.15
E _{gas}	-2273.44	-2273.44
E _{solv}	-2273.50	-2273.50
G	-2273.10	-2273.17
ZPE	282.431	282.431
H _{vib}	21.461	55.867
S _{trans}	45.471	48.021
S _{rot}	37.686	39.216
S _{vib}	138.480	225.262
solv	-42.9	-42.9

Table S316. $[\text{Rh}^{\text{III}}(\text{bisq}^{\text{Me2}})(\text{Me}_{\text{ax}})(\text{TFA}_{\text{eq}})(\text{TFAH}_{\text{eq}})]^+$ Cartesian coordinates

Atom	x	y	z
Rh1	-1.18533	0.479094	-1.47543

N2	-1.7359	-0.99211	-0.10578
C3	-1.88596	-2.26837	-0.44326
C4	-2.53031	-3.20362	0.388236
C5	-3.06682	-2.77511	1.580717
C6	-5.59921	2.535695	-1.39475
C7	-5.41046	1.253583	-1.84841
C8	-4.12302	0.700405	-1.77929
N9	-3.07021	1.340078	-1.27347
H10	-1.50154	-2.56227	-1.41182
H11	-2.62064	-4.23187	0.056954
H12	-3.62018	-3.45672	2.220371
H13	-3.94536	-0.29029	-2.17164
O14	0.60644	-0.66055	-1.56374
C15	1.825624	-0.5318	-1.76552
O16	2.466343	0.462891	-2.23287
C17	2.733143	-1.73571	-1.41283
F18	3.370344	-2.15976	-2.50903
F19	3.640889	-1.3563	-0.49834
F20	2.014712	-2.74465	-0.90966
O21	-0.92094	2.043795	-2.83749
C22	0.094711	2.617687	-3.32106
O23	1.306119	2.341584	-3.21977
C24	-0.25892	3.902943	-4.11496
F25	-0.57046	4.877721	-3.22733
F26	0.760695	4.32266	-4.86106
F27	-1.32332	3.702669	-4.90389
H28	1.854831	1.283814	-2.61729
C29	-3.2387	2.599175	-0.72358
C30	-4.51805	3.241146	-0.81797
C31	-4.68778	4.561673	-0.33002
C32	-3.63611	5.22285	0.253153
C33	-2.3952	4.570164	0.395131
C34	-2.1715	3.279035	-0.06252
H35	-5.66196	5.031276	-0.42637
H36	-3.75578	6.235075	0.625511
H37	-1.58389	5.084404	0.901094
C38	-2.12144	-0.56773	1.149109
C39	-2.87246	-1.43533	1.999301
C40	-3.35758	-0.93786	3.236232
C41	-3.06728	0.348685	3.624839

C42	-2.22804	1.159856	2.827226
C43	-1.73695	0.723625	1.608913
H44	-3.94239	-1.59399	3.87408
H45	-3.43525	0.731293	4.571452
H46	-1.92124	2.133742	3.197372
H47	-6.21506	0.670464	-2.28118
H48	-6.56944	3.019133	-1.46323
C49	-0.82958	2.684452	0.190661
C50	-0.64159	1.490651	0.923815
C51	0.680952	1.103786	1.245204
C52	1.799861	1.843082	0.876327
C53	1.606813	3.039575	0.138465
C54	0.310285	3.426989	-0.1834
H55	0.819625	0.202685	1.836966
H58	0.162204	4.331035	-0.76652
C59	-1.72424	-0.57016	-3.1633
H60	-2.19955	0.143463	-3.83618
H61	-0.798	-0.95266	-3.59476
H62	-2.39707	-1.39424	-2.91896
C62	2.783284	3.867622	-0.31225
H63	2.459826	4.775367	-0.8262
H64	3.414858	4.161318	0.53367
H65	3.419377	3.301169	-1.00261
C65	3.184833	1.381186	1.258152
H66	3.707337	2.138164	1.85395
H67	3.150321	0.458336	1.841919
H68	3.799245	1.192465	0.371195

Table S317.

$[\text{Rh}^{\text{III}}(\text{bisq}^{\text{Me2}})(\text{Me}_{\text{ax}})(\text{TFA}_{\text{eq}})(\text{TFAH}_{\text{eq}})]^+$
thermodynamic values

Temp	298.15	498.15
E_{gas}	-2313.95	-2313.95
E_{solv}	-2314.01	-2314.01
G	-2313.56	-2313.64
ZPE	312.193	312.193
H_{vib}	22.942	59.584
S_{trans}	45.540	48.090
S_{rot}	37.808	39.339

S_{vib}	148.393	240.811
solv	-39.1	-39.1

Table S318.

$[\text{Rh}^{\text{III}}(\text{bisq}^{\text{Me2}})(\text{Me}_{\text{eq}})(\text{TFA}_{\text{ax}})(\text{TFAH}_{\text{eq}})]^+$ Cartesian coordinates

Atom	x	y	z
Rh1	-1.48126	0.349421	-2.00079
N2	-2.13781	-1.03778	-0.1438
C3	-2.8659	-2.08753	-0.50553
C4	-3.34003	-3.06716	0.389373
C5	-3.02549	-2.9499	1.719442
C6	-6.11551	1.669407	-1.83019
C7	-5.63724	1.041127	-2.95671
C8	-4.27053	0.709487	-3.03639
N9	-3.41225	1.013817	-2.06877
H10	-3.07813	-2.18002	-1.56429
H11	-3.92932	-3.89512	0.010585
H12	-3.35593	-3.68845	2.444791
O13	-2.13301	-1.19442	-3.21341
H14	-3.87893	0.150579	-3.87564
O15	0.547391	-0.25805	-1.71903
C16	1.51497	-0.62264	-2.40269
O17	1.550564	-1.02828	-3.61377
C18	2.922723	-0.56323	-1.7586
F19	3.633793	-1.64692	-2.06427
F20	3.560006	0.526397	-2.23491
F21	2.839971	-0.45624	-0.42721
H22	0.61136	-1.22336	-4.06134
C23	-1.64767	-1.79906	-4.22447
O24	-0.51572	-1.74386	-4.72104
C25	-2.70823	-2.70312	-4.90734
F26	-2.19302	-3.41717	-5.89956
F27	-3.25472	-3.53717	-4.00245
F28	-3.69457	-1.91929	-5.39978
C29	-3.84318	1.697279	-0.95375
C30	-5.22354	2.0101	-0.78329
C31	-5.63746	2.63261	0.421826
C32	-4.71388	2.933433	1.396438

C33	-3.34178	2.6621	1.192479
C34	-2.8904	2.061011	0.029996
H35	-6.68954	2.862431	0.560978
H36	-5.03037	3.403716	2.322003
H37	-2.62412	2.949248	1.954977
C38	-1.82602	-0.88234	1.187701
C39	-2.249	-1.84956	2.157456
C40	-1.88305	-1.70535	3.519797
C41	-1.1134	-0.64124	3.921478
C42	-0.69899	0.317971	2.975236
C43	-1.04299	0.231568	1.633277
H44	-2.21863	-2.45335	4.232452
H45	-0.82709	-0.52805	4.962194
H46	-0.10796	1.16567	3.30912
H47	-6.29081	0.769785	-3.77796
H48	-7.17063	1.907237	-1.72899
C49	-1.41812	1.921252	-0.24079
C50	-0.5509	1.267399	0.697887
C51	0.789918	1.625593	0.722009
C52	1.344957	2.59614	-0.13411
C53	0.527351	3.209676	-1.1001
C54	-0.83171	2.871783	-1.12428
H55	1.449786	1.11183	1.413775
H58	-1.49466	3.430513	-1.77734
C59	-0.99403	1.428583	-3.70553
H60	-1.05829	0.752089	-4.55811
H61	-1.69122	2.257738	-3.83839
H62	0.024906	1.806067	-3.60609
C62	1.076531	4.240273	-2.05622
H63	0.299617	4.619078	-2.72437
H64	1.503979	5.095551	-1.52013
H65	1.879586	3.824388	-2.67619
C65	2.805395	2.94295	-0.01677
H66	2.9474	4.021016	0.118614
H67	3.271598	2.428065	0.825683
H68	3.349585	2.660112	-0.92442

Table S319.

$[\text{Rh}^{\text{III}}(\text{bisq}^{\text{Me}_2})(\text{Me}_{\text{eq}})(\text{TFA}_{\text{ax}})(\text{TFAH}_{\text{eq}})]^+$
thermodynamic values

Temp	298.15	498.15
E_{gas}	-2313.94	-2313.94
E_{solv}	-2314.00	-2314.00
G	-2313.55	-2313.63
ZPE	312.557	312.557
H_{vib}	23.052	59.710
S_{trans}	45.540	48.090
S_{rot}	37.929	39.459
S_{vib}	149.725	242.193
solv	-37.9	-37.9

Table S320. $\text{Rh}^{\text{III}}(\text{bisq}^{\text{Me}_2})(\text{Me}_{\text{ax}})(\text{TFA})_2$ Cartesian coordinates

Atom	x	y	z
Rh1	-1.80397	0.270421	-1.7813
N2	-2.54777	-0.80142	-0.10985
C3	-3.46983	-1.7436	-0.2657
C4	-3.84423	-2.64148	0.751036
C5	-3.19882	-2.57172	1.960409
C6	-6.40037	1.864186	-1.75011
C7	-5.85138	1.42692	-2.93128
C8	-4.47415	1.118845	-2.98014
N9	-3.67135	1.278035	-1.93362
H10	-3.91596	-1.8195	-1.24898
H11	-4.604	-3.38806	0.547639
H12	-3.42133	-3.27423	2.759039
H13	-3.99959	0.743978	-3.88181
O14	-0.05411	-0.72749	-1.40918
C15	0.808553	-1.08758	-2.30682
O16	0.74749	-1.0987	-3.52196
C17	2.106492	-1.58191	-1.60422
F18	3.022025	-2.00509	-2.48318
F19	2.675335	-0.5847	-0.87378
F20	1.849275	-2.5992	-0.75221
O21	-0.866	1.392885	-3.19869
C22	-1.21747	1.568541	-4.4195
O23	-2.2123	1.188516	-5.02941
C24	-0.20933	2.474373	-5.18016
F25	-0.09733	2.113251	-6.46511

F26	-0.65721	3.758789	-5.15134
F27	1.025791	2.478751	-4.64005
C28	-4.15983	1.875586	-0.78959
C29	-5.55864	2.109914	-0.63484
C30	-6.04464	2.607431	0.601826
C31	-5.16862	2.907594	1.618329
C32	-3.77502	2.784842	1.414782
C33	-3.25442	2.29452	0.23132
H34	-7.11355	2.762345	0.721051
H35	-5.53862	3.290005	2.564972
H36	-3.09084	3.122677	2.187684
C37	-1.9524	-0.63646	1.124213
C38	-2.22922	-1.56434	2.180089
C39	-1.54058	-1.45934	3.414464
C40	-0.62504	-0.45477	3.607856
C41	-0.4054	0.498768	2.592627
C42	-1.05351	0.447697	1.368055
H43	-1.75247	-2.18549	4.194231
H44	-0.0861	-0.37159	4.54672
H45	0.280638	1.320212	2.775607
H46	-6.4553	1.276025	-3.81952
H47	-7.4674	2.051542	-1.66108
C48	-1.79397	2.411031	-0.08165
C49	-0.78618	1.548975	0.399644
C50	0.552575	1.827991	0.055817
C51	0.91384	2.903923	-0.74585
C52	-0.09178	3.79731	-1.18569
C53	-1.41197	3.533304	-0.84255
H54	1.316109	1.125509	0.370591
H57	-2.19039	4.207884	-1.18996
C58	-2.30947	-1.24379	-3.07072
H59	-1.76908	-1.07013	-3.99632
H60	-1.98349	-2.1747	-2.60194
H61	-3.39029	-1.24672	-3.24029
C61	0.244521	4.983179	-2.05485
H62	-0.6206	5.640537	-2.17694
H63	1.065725	5.575694	-1.63625
H64	0.553993	4.655174	-3.05291
C64	2.34573	3.07767	-1.18733
H65	2.405403	3.061854	-2.28172

H66	2.767651	4.033693	-0.85325
H67	2.97609	2.270182	-0.80844

Table S321. Rh^{III}(bisq^{Me2})(Me_{ax})(TFA)₂
thermodynamic values

Temp	298.15	498.15
E_{gas}	-2313.55	-2313.55
E_{solv}	-2313.58	-2313.58
G	-2313.15	-2313.22
ZPE	305.281	305.281
H_{vib}	22.931	59.440
S_{trans}	45.536	48.086
S_{rot}	37.767	39.297
S_{vib}	148.556	240.661
solv	-19.8	-19.8

Table S322. Rh^{III}(bisq^{Me2})(Me_{eq})(TFA)₂ Cartesian
coordinates

Atom	x	y	z
Rh1	-1.48837	0.521181	-2.10441
N2	-2.29548	-0.87877	-0.12741
C3	-3.08558	-1.86559	-0.51465
C4	-3.58758	-2.8617	0.351214
C5	-3.23585	-2.81792	1.676112
C6	-6.1721	1.772248	-1.7991
C7	-5.70544	1.165698	-2.94118
C8	-4.33252	0.85819	-3.04738
N9	-3.46464	1.163348	-2.09273
H10	-3.34687	-1.8857	-1.56651
H11	-4.22281	-3.64564	-0.04727
H12	-3.58314	-3.5723	2.377694
O13	-2.1034	-0.94394	-3.37467
H14	-3.9275	0.31506	-3.89429
O15	0.453626	-0.03497	-1.87626
C16	1.236414	-0.49252	-2.79636
O17	1.044867	-0.69303	-3.98301
C18	2.668904	-0.73804	-2.24144
F19	3.214926	-1.84543	-2.75952

F20	3.466968	0.311792	-2.59407
F21	2.728825	-0.83545	-0.89777
C22	-1.65122	-2.16555	-3.36873
O23	-0.85839	-2.71645	-2.63362
C24	-2.42051	-2.98924	-4.43823
F25	-1.87437	-4.1928	-4.63193
F26	-3.69855	-3.18105	-4.00116
F27	-2.49593	-2.36339	-5.62667
C28	-3.88655	1.813334	-0.95696
C29	-5.26803	2.10714	-0.75866
C30	-5.67808	2.692605	0.465912
C31	-4.74834	2.97268	1.440204
C32	-3.37713	2.712183	1.219257
C33	-2.92545	2.150384	0.037529
H34	-6.73212	2.905329	0.621318
H35	-5.06078	3.411505	2.383083
H36	-2.65587	2.969312	1.988831
C37	-1.95641	-0.79194	1.197701
C38	-2.40434	-1.76979	2.143553
C39	-2.01582	-1.67555	3.503764
C40	-1.20784	-0.64575	3.921086
C41	-0.77277	0.327566	2.996696
C42	-1.13069	0.2852	1.65831
H43	-2.36719	-2.43044	4.202438
H44	-0.90641	-0.56995	4.961643
H45	-0.14817	1.145826	3.343467
H46	-6.37159	0.894091	-3.75273
H47	-7.22872	1.993971	-1.67495
C48	-1.45387	1.99206	-0.2088
C49	-0.60815	1.303634	0.71807
C50	0.75494	1.555975	0.68594
C51	1.354492	2.45543	-0.21663
C52	0.551828	3.103591	-1.15836
C53	-0.83703	2.855199	-1.14662
H54	1.39871	0.995085	1.357107
H57	-1.4745	3.457291	-1.78621
C58	-1.07758	1.562474	-3.83355
H59	-1.15988	0.828966	-4.63322
H60	-1.80318	2.373402	-3.95099
H61	-0.06094	1.950026	-3.7824

C61	2.849217	2.651249	-0.18465
H62	3.317675	2.154208	-1.04146
H63	3.123894	3.710854	-0.22581
H64	3.282963	2.221389	0.721762
C64	1.138578	4.054863	-2.17186
H65	0.362891	4.487314	-2.80857
H66	1.676695	4.878972	-1.68786
H67	1.858566	3.542875	-2.82152

Table S323. Rh^{III}(bisq^{Me2})(Me_{eq})(TFA)₂
thermodynamic values

Temp	298.15	498.15
E_{gas}	-2313.54	-2313.54
E_{solv}	-2313.57	-2313.57
G	-2313.14	-2313.21
ZPE	304.809	304.809
H_{vib}	23.161	59.726
S_{trans}	45.536	48.086
S_{rot}	37.841	39.371
S_{vib}	150.117	242.368
solv	-19.4	-19.4

Table S324. [Rh^{IV}(bisq^{Me2})(Me_{ax})(TFA)₂]⁺
Cartesian coordinates

Atom	x	y	z
Rh1	-1.8198	0.240991	-1.78155
N2	-2.55424	-0.81514	-0.11714
C3	-3.48309	-1.75938	-0.27741
C4	-3.87174	-2.63949	0.740804
C5	-3.23876	-2.55339	1.96069
C6	-6.41758	1.808079	-1.69732
C7	-5.89991	1.315	-2.87414
C8	-4.53231	0.993808	-2.93584
N9	-3.7031	1.191695	-1.91011
H10	-3.92477	-1.84051	-1.26185
H11	-4.63116	-3.38629	0.539626
H12	-3.47587	-3.24599	2.76335
H13	-4.09191	0.57662	-3.83316

O14	-0.09193	-0.7186	-1.46045
C15	0.814741	-0.90325	-2.38505
O16	0.754806	-0.65022	-3.57353
C17	2.115144	-1.48317	-1.76236
F18	2.982663	-1.83966	-2.70416
F19	2.694252	-0.54658	-0.97594
F20	1.83274	-2.55093	-0.99854
O21	-0.96635	1.392672	-3.13588
C22	-1.23277	1.515984	-4.41619
O23	-2.21729	1.121421	-5.0098
C24	-0.15891	2.36509	-5.14595
F25	-0.06372	2.00419	-6.42321
F26	-0.53729	3.663035	-5.08892
F27	1.048654	2.26451	-4.56981
C28	-4.15844	1.838644	-0.77544
C29	-5.5541	2.091437	-0.61023
C30	-6.01724	2.654319	0.60691
C31	-5.12278	2.997512	1.594231
C32	-3.73506	2.849448	1.374801
C33	-3.23515	2.291224	0.209876
H34	-7.0819	2.827223	0.73373
H35	-5.47347	3.432993	2.524493
H36	-3.03638	3.220767	2.118833
C37	-1.9659	-0.63468	1.121392
C38	-2.26734	-1.55138	2.181371
C39	-1.58946	-1.44522	3.422763
C40	-0.65371	-0.45718	3.615165
C41	-0.40332	0.477559	2.592031
C42	-1.04924	0.433057	1.36122
H43	-1.82032	-2.15908	4.207654
H44	-0.12233	-0.37507	4.557766
H45	0.298115	1.28577	2.775108
H46	-6.52356	1.136227	-3.74266
H47	-7.48016	2.01026	-1.59692
C48	-1.77385	2.384407	-0.11503
C49	-0.76643	1.529569	0.395795
C50	0.581078	1.820016	0.083485
C51	0.954304	2.897968	-0.71028
C52	-0.05191	3.780874	-1.18319
C53	-1.37994	3.506708	-0.87015

H54	1.346652	1.137665	0.436884
H57	-2.15211	4.18414	-1.22468
C58	-2.27678	-1.2878	-3.10981
H59	-1.72571	-1.09231	-4.02381
H60	-1.93177	-2.19788	-2.61913
H61	-3.35229	-1.30273	-3.28173
C61	0.297619	4.975842	-2.03117
H62	-0.57502	5.610515	-2.20274
H63	1.077178	5.587424	-1.56426
H64	0.677787	4.660969	-3.00932
C64	2.398762	3.103882	-1.08937
H65	2.510793	3.108385	-2.1798
H66	2.780845	4.064622	-0.72482
H67	3.032646	2.309274	-0.69054

Table S325. $[\text{Rh}^{\text{IV}}(\text{bisq}^{\text{Me}_2})(\text{Me}_{\text{ax}})(\text{TFA})_2]^+$
thermodynamic values

Temp	298.15	498.15
E_{gas}	-2313.27	-2313.27
E_{solv}	-2313.35	-2313.35
G	-2312.91	-2312.98
ZPE	305.151	305.151
H_{vib}	22.914	59.465
S_{trans}	45.536	48.086
S_{rot}	37.736	39.266
S_{vib}	148.142	240.350
solv	-44.9	-44.9

Table S326. $[\text{Rh}^{\text{IV}}(\text{bisq}^{\text{Me}_2})(\text{Me}_{\text{eq}})(\text{TFA})_2]^+$
Cartesian coordinates

Atom	x	y	z
Rh1	-1.48283	0.544656	-2.10481
N2	-2.37425	-0.87732	-0.17886
C3	-3.23911	-1.81024	-0.55039
C4	-3.75346	-2.7959	0.315783
C5	-3.33738	-2.80344	1.625271
C6	-6.17046	1.865251	-1.88924
C7	-5.69195	1.290462	-3.04507

C8	-4.32373	0.960798	-3.13673
N9	-3.47182	1.218468	-2.15319
H10	-3.53921	-1.7972	-1.5926
H11	-4.44601	-3.53696	-0.06774
H12	-3.68612	-3.5591	2.323735
O13	-2.11406	-0.97427	-3.23649
H14	-3.91569	0.449099	-4.00178
O15	0.443843	-0.0255	-1.83409
C16	1.205422	-0.54325	-2.7556
O17	0.957639	-0.79517	-3.91749
C18	2.648907	-0.75954	-2.22163
F19	3.222309	-1.82302	-2.77683
F20	3.39123	0.337933	-2.54566
F21	2.704204	-0.88926	-0.88167
C22	-1.60623	-2.195	-3.21708
O23	-0.84149	-2.69403	-2.42772
C24	-2.27639	-3.02955	-4.34168
F25	-1.70173	-4.22109	-4.46871
F26	-3.58091	-3.21538	-4.008
F27	-2.24005	-2.39545	-5.52291
C28	-3.90826	1.823966	-1.00073
C29	-5.28322	2.140687	-0.81703
C30	-5.69665	2.68595	0.426634
C31	-4.77753	2.897701	1.428952
C32	-3.40846	2.60432	1.225947
C33	-2.96088	2.081973	0.025776
H34	-6.74573	2.924032	0.575679
H35	-5.09571	3.30802	2.382072
H36	-2.69823	2.81151	2.020794
C37	-1.98539	-0.83117	1.128385
C38	-2.4324	-1.80885	2.070144
C39	-1.94821	-1.7821	3.403474
C40	-1.04052	-0.82256	3.803319
C41	-0.59881	0.144273	2.887132
C42	-1.07112	0.183661	1.572492
H43	-2.29334	-2.54109	4.100198
H44	-0.67035	-0.8068	4.823165
H45	0.091968	0.911384	3.22327
H46	-6.34666	1.064496	-3.87922
H47	-7.22481	2.104352	-1.7821

C48	-1.50175	1.896837	-0.26222
C49	-0.61094	1.231182	0.666849
C50	0.751091	1.569285	0.65284
C51	1.311421	2.454081	-0.26607
C52	0.467429	3.050365	-1.24495
C53	-0.91486	2.764671	-1.2221
H54	1.416082	1.05029	1.335559
H57	-1.57186	3.374956	-1.83268
C58	-1.0652	1.481778	-3.91292
H59	-1.17135	0.685763	-4.64489
H60	-1.78505	2.289369	-4.05304
H61	-0.03861	1.838785	-3.87983
C61	2.791136	2.709371	-0.2555
H62	3.265114	2.19701	-1.10113
H63	3.021727	3.775701	-0.34386
H64	3.250579	2.331031	0.659817
C64	1.023121	3.991274	-2.27024
H65	0.248049	4.367854	-2.93974
H66	1.514357	4.849385	-1.79526
H67	1.791614	3.490982	-2.87388

Table S327. $[\text{Rh}^{\text{IV}}(\text{bisq}^{\text{Me}_2})(\text{Me}_{\text{eq}})(\text{TFA})_2]^+$
thermodynamic values

Temp	298.15	498.15
E_{gas}	-2313.27	-2313.27
E_{solv}	-2313.35	-2313.35
G	-2312.91	-2312.99
ZPE	304.751	304.751
H_{vib}	22.524	58.742
S_{trans}	45.536	48.086
S_{rot}	37.790	39.320
S_{vib}	148.836	241.216
solv	-48.5	-48.5

Table S328. $[\text{Rh}^{\text{I-III}}(\text{bisq}^{\text{Me}_2})(\text{Me}_{\text{ax}}\cdots\text{H}_{\text{eq}})(\text{TFA}_{\text{eq}})]^{\ddagger}$
Cartesian coordinates

Atom	x	y	z
Rh1	-1.55948	0.283301	-2.06725

N2	-2.35363	-1.01845	0.198265
C3	-3.1141	-2.06317	-0.06112
C4	-3.57271	-2.97169	0.920058
C5	-3.19475	-2.76633	2.223931
C6	-6.21881	1.696255	-1.87878
C7	-5.74645	1.099528	-3.02354
C8	-4.38344	0.754581	-3.10842
N9	-3.50777	0.999182	-2.1384
H10	-3.38303	-2.21231	-1.10575
H11	-4.19895	-3.8103	0.632429
H12	-3.51177	-3.4422	3.014506
H13	-3.99826	0.244971	-3.98275
O14	0.291408	-0.53956	-1.76428
C15	1.325054	-0.23163	-2.46263
O16	1.437123	0.490865	-3.44616
C17	2.593894	-0.93902	-1.90881
F18	3.718566	-0.39858	-2.41474
F19	2.679444	-0.84574	-0.56176
F20	2.592606	-2.25281	-2.22477
H21	-1.33795	0.314572	-3.62622
C22	-3.94045	1.662397	-1.00593
C23	-5.31827	1.990898	-0.82548
C24	-5.73333	2.583137	0.394374
C25	-4.8106	2.848911	1.378742
C26	-3.44169	2.570622	1.170832
C27	-2.9847	1.993948	-0.00284
H28	-6.78506	2.817462	0.53389
H29	-5.12606	3.297331	2.3164
H30	-2.72276	2.830739	1.941049
C31	-1.97379	-0.7829	1.489509
C32	-2.37141	-1.65939	2.551165
C33	-1.93862	-1.41285	3.878392
C34	-1.12652	-0.33714	4.145801
C35	-0.73242	0.53175	3.105075
C36	-1.13744	0.346255	1.791791
H37	-2.25686	-2.08642	4.670047
H38	-0.78841	-0.14394	5.159851
H39	-0.10019	1.38365	3.338309
H40	-6.40214	0.867877	-3.8561
H41	-7.27012	1.947332	-1.76706

C42	-1.52276	1.821112	-0.25413
C43	-0.64958	1.254653	0.726472
C44	0.712268	1.511498	0.631401
C45	1.280057	2.303145	-0.38691
C46	0.450386	2.826371	-1.38159
C47	-0.93786	2.564014	-1.31617
H48	1.378155	1.035535	1.345327
H49	-1.59097	3.111385	-1.98851
C50	-1.75524	-1.10413	-3.73657
H51	-2.3393	-0.89011	-4.63711
H52	-0.79279	-1.52616	-4.02278
H53	-2.30704	-1.83973	-3.13844
C54	1.002851	3.626462	-2.53291
H55	0.200856	4.101577	-3.10502
H56	1.691698	4.409135	-2.19573
H57	1.549344	2.961123	-3.21118
C58	2.7758	2.509305	-0.42353
H59	3.038881	3.573359	-0.45411
H60	3.256088	2.067758	0.453467
H61	3.21434	2.043486	-1.31358

Table S329. $[\text{Rh}^{\text{I-III}}(\text{bisq}^{\text{Me2}})(\text{Me}_{\text{ax}}\cdots\text{H}_{\text{eq}})(\text{TFA}_{\text{eq}})]^{\dagger}$
thermodynamic values

Temp	298.15	498.15
E_{gas}	-1787.95	-1787.95
E_{solv}	-1787.97	-1787.97
G	-1787.55	-1787.61
ZPE	289.731	289.731
H_{vib}	19.056	50.335
S_{trans}	45.019	47.569
S_{rot}	36.979	38.509
S_{vib}	122.842	201.670
solv	-14.2	-14.2

Table S330. $[\text{Rh}^{\text{I-III}}(\text{bisq}^{\text{Me2}})(\text{Me}_{\text{eq}}\cdots\text{H}_{\text{ax}})(\text{TFA}_{\text{eq}})]^{\dagger}$
Cartesian coordinates

Atom	x	y	z
Rh1	-1.45045	0.222759	-1.66791

N2	-1.54418	-1.19239	0.054802
C3	-1.64095	-2.47876	-0.25994
C4	-2.14671	-3.45005	0.63391
C5	-2.585	-3.05548	1.874656
C6	-6.19065	1.296169	-1.02773
C7	-5.74745	0.16056	-1.65787
C8	-4.36175	-0.06174	-1.75219
N9	-3.44046	0.756018	-1.24417
H10	-1.29675	-2.74175	-1.25737
H11	-2.19825	-4.48601	0.315264
H12	-3.01126	-3.76918	2.575489
H13	-1.82153	-0.01015	-3.1673
H14	-3.97661	-0.9305	-2.27307
O15	0.511009	-0.21563	-2.11373
C16	0.878043	-1.36113	-2.55767
O17	0.235945	-2.3913	-2.74695
C18	2.390394	-1.35332	-2.91388
F19	2.856676	-2.58609	-3.16515
F20	2.616534	-0.59707	-4.01237
F21	3.139437	-0.83556	-1.90907
C22	-3.85298	1.885681	-0.55995
C23	-5.25146	2.19509	-0.46711
C24	-5.67855	3.389052	0.167639
C25	-4.75741	4.257138	0.69778
C26	-3.38468	3.939997	0.637348
C27	-2.90941	2.77963	0.045236
H28	-6.74338	3.599402	0.218381
H29	-5.07638	5.177588	1.177791
H30	-2.66335	4.615276	1.088267
C31	-1.89087	-0.784	1.318985
C32	-2.46552	-1.69574	2.258624
C33	-2.88001	-1.22119	3.529166
C34	-2.7067	0.101134	3.86257
C35	-2.08135	0.986332	2.95499
C36	-1.66341	0.57218	1.702787
H37	-3.32566	-1.92127	4.23127
H38	-3.02202	0.467258	4.835363
H39	-1.89709	2.013915	3.254811
H40	-6.43192	-0.55611	-2.09882
H41	-7.25052	1.523959	-0.95182

C42	-1.43669	2.541285	0.084966
C43	-0.86554	1.495872	0.836254
C44	0.532185	1.379899	0.868308
C45	1.378922	2.248842	0.182719
C46	0.807886	3.325085	-0.53101
C47	-0.58057	3.457431	-0.54895
H48	0.969181	0.566868	1.442298
H49	-1.0247	4.27524	-1.11125
C50	-1.45184	1.414492	-3.48167
H51	-0.8881	1.063132	-4.34978
H52	-2.42465	1.797774	-3.79939
H53	-0.87231	2.213115	-3.00902
C54	1.675071	4.302052	-1.28936
H55	2.382132	4.817379	-0.62749
H56	2.271531	3.790553	-2.05399
H57	1.070066	5.062831	-1.79026
C58	2.866621	1.996538	0.177736
H59	3.447587	2.916913	0.296522
H60	3.150757	1.310185	0.980387
H61	3.167509	1.529657	-0.76778

Table S331. $[\text{Rh}^{\text{I-III}}(\text{bisq}^{\text{Me2}})(\text{Me}_{\text{eq}}\cdots\text{H}_{\text{ax}})(\text{TFA}_{\text{eq}})]^{\dagger}$
thermodynamic values

Temp	298.15	498.15
E _{gas}	-1787.95	-1787.95
E _{solv}	-1787.97	-1787.97
G	-1787.55	-1787.62
ZPE	290.172	290.172
H _{vib}	19.056	50.256
S _{trans}	45.019	47.569
S _{rot}	37.060	38.590
S _{vib}	123.000	201.628
solv	-14.3	-14.3

Table S332. $[\text{Rh}^{\text{I-III}}(\text{bisq}^{\text{Me2}})(\text{Me}_{\text{eq}}\cdots\text{H}_{\text{eq}})(\text{TFA}_{\text{ax}})]^{\dagger}$
Cartesian coordinates

Atom	x	y	z
Rh1	-1.37751	0.36378	-1.90934

N2	-2.33255	-0.92098	-0.42167
C3	-3.10489	-1.95563	-0.71786
C4	-3.60245	-2.83692	0.267323
C5	-3.26987	-2.6317	1.585633
C6	-6.47172	1.559125	-1.55332
C7	-6.09029	0.875602	-2.6835
C8	-4.70785	0.684365	-2.93188
N9	-3.76652	1.155649	-2.14058
H10	-3.30817	-2.10447	-1.77374
H11	-4.23098	-3.66822	-0.03486
H12	-3.62844	-3.29862	2.365445
O13	-1.98567	-1.02343	-3.29883
H14	-4.36143	0.108648	-3.7885
H15	0.112362	0.339246	-2.39362
C16	-1.24874	-1.80964	-4.01212
O17	-0.03807	-1.93473	-4.0714
C18	-2.16513	-2.70641	-4.89201
F19	-1.46774	-3.53622	-5.67601
F20	-2.9806	-3.46577	-4.1139
F21	-2.96406	-1.95745	-5.68798
C22	-4.11612	1.845273	-1.01768
C23	-5.4836	2.063782	-0.66663
C24	-5.78884	2.751252	0.534969
C25	-4.77239	3.197776	1.348125
C26	-3.41947	2.991837	0.988948
C27	-3.07185	2.327908	-0.17476
H28	-6.8298	2.915704	0.802154
H29	-5.00332	3.721893	2.27112
H30	-2.63434	3.371635	1.63635
C31	-1.98689	-0.68848	0.882716
C32	-2.43171	-1.54176	1.934478
C33	-1.99591	-1.28291	3.258932
C34	-1.14614	-0.23044	3.51006
C35	-0.71285	0.611078	2.459459
C36	-1.12656	0.409539	1.153716
H37	-2.33075	-1.93437	4.061737
H38	-0.80341	-0.03624	4.522236
H39	-0.05079	1.443308	2.681077
H40	-6.82349	0.473087	-3.37548
H41	-7.52267	1.714431	-1.32114

C42	-1.61684	2.235171	-0.57046
C43	-0.68683	1.336991	0.061105
C44	0.706036	1.686103	0.020999
C45	1.182851	2.826237	-0.58305
C46	0.253348	3.725513	-1.20314
C47	-1.08762	3.416135	-1.18587
H48	1.402745	1.010318	0.510075
H49	-1.79825	4.110492	-1.62683
C50	-0.18757	1.314838	-3.47911
H51	0.153282	0.626663	-4.25229
H52	-1.03067	1.900233	-3.85702
H53	0.613879	1.999189	-3.19644
C54	0.734552	4.997048	-1.86002
H55	1.274926	5.639674	-1.15407
H56	1.42431	4.787158	-2.68666
H57	-0.10314	5.571732	-2.26387
C58	2.6627	3.125456	-0.59433
H59	2.885319	4.094479	-0.13102
H60	3.223353	2.357617	-0.05495
H61	3.05632	3.167408	-1.61751

Table S333. $[\text{Rh}^{\text{I-III}}(\text{bisq}^{\text{Me2}})(\text{Me}_{\text{eq}}\cdots\text{H}_{\text{eq}})(\text{TFA}_{\text{ax}})]^{\dagger}$
thermodynamic values

Temp	298.15	498.15
E_{gas}	-1787.93	-1787.93
E_{solv}	-1787.96	-1787.96
G	-1787.54	-1787.60
ZPE	289.682	289.682
H_{vib}	19.095	50.387
S_{trans}	45.019	47.569
S_{rot}	37.122	38.652
S_{vib}	122.910	201.774
solv	-14.1	-14.1

Table S334. $[\text{Rh}^{\text{I-III}}(\text{bisq}^{\text{Me2}})(\text{H}_{\text{ax}}\cdots\text{TFA}_{\text{eq}})(\text{Me}_{\text{eq}})]^{\dagger}$
Cartesian coordinates

Atom	x	y	z
Rh1	-1.41358	0.486194	-1.93288

N2	-2.12198	-0.70998	-0.05908
C3	-2.88077	-1.74807	-0.38664
C4	-3.34014	-2.71426	0.531929
C5	-2.95375	-2.60489	1.844604
C6	-6.10886	1.62494	-1.94559
C7	-5.49746	1.157771	-3.08375
C8	-4.1017	0.965724	-3.08375
N9	-3.31969	1.241445	-2.03849
H10	-3.13081	-1.83025	-1.43983
H11	-3.96642	-3.52989	0.185664
H12	-3.25501	-3.34061	2.586038
H13	-1.18329	-1.06743	-3.0673
H14	-3.59785	0.543074	-3.94374
O15	0.557052	-0.43978	-1.83587
C16	0.595831	-1.41777	-2.58958
O17	-0.39737	-1.83675	-3.30469
C18	1.887625	-2.23843	-2.72898
F19	1.663529	-3.52001	-2.38325
F20	2.320358	-2.21505	-4.00151
F21	2.856343	-1.75481	-1.94389
C28	-3.89285	1.834208	-0.9223
C29	-5.31466	1.976313	-0.82529
C30	-5.89499	2.468637	0.372105
C31	-5.09761	2.836159	1.428285
C32	-3.69376	2.776268	1.299978
C33	-3.07508	2.305486	0.15272
H34	-6.977	2.553139	0.431456
H35	-5.53736	3.208962	2.348961
H36	-3.07067	3.141532	2.110562
C37	-1.77567	-0.53951	1.260103
C38	-2.14774	-1.51236	2.247275
C39	-1.71191	-1.37456	3.589307
C40	-0.93977	-0.29935	3.952754
C41	-0.61388	0.685481	2.99714
C42	-1.02061	0.607869	1.672189
H43	-1.99902	-2.13168	4.31423
H44	-0.59409	-0.1883	4.976494
H45	-0.04175	1.554323	3.308519
H46	-6.06718	0.901124	-3.9708
H47	-7.18793	1.741231	-1.88791

C48	-1.58994	2.48042	0.034559
C49	-0.64693	1.729616	0.767914
C50	0.699974	2.125342	0.724102
C51	1.143252	3.231361	0.000852
C52	0.195664	4.000609	-0.70646
C53	-1.14242	3.611062	-0.66903
H54	1.429208	1.527559	1.264495
H57	-1.87767	4.208831	-1.20175
C58	-0.83292	1.445333	-3.65935
H59	-0.32432	0.781703	-4.3738
H60	-1.67756	1.912026	-4.18672
H61	-0.12809	2.241963	-3.38116
C55	2.608642	3.595775	-0.01095
H56	2.783541	4.586696	0.4272
H58	3.200283	2.871012	0.5548
H62	3.007974	3.627405	-1.03171
C59	0.611137	5.226852	-1.48423
H63	1.129014	5.955727	-0.84806
H64	1.301024	4.971008	-2.2978
H65	-0.25462	5.72526	-1.92866

Table S335. $[\text{Rh}^{\text{I-III}}(\text{bisq}^{\text{Me2}})(\text{H}_{\text{ax}}\cdots\text{TFA}_{\text{eq}})(\text{Me}_{\text{eq}})]^{\dagger}$
thermodynamic values

Temp	298.15	498.15
E _{gas}	-1787.93	-1787.93
E _{solv}	-1787.95	-1787.95
G	-1787.53	-1787.59
ZPE	289.429	289.429
H _{vib}	18.867	50.028
S _{trans}	45.019	47.569
S _{rot}	37.141	38.671
S _{vib}	121.847	200.358
solv	-9.7	-9.7

Table S336. $[\text{Rh}^{\text{I-III}}(\text{bisq}^{\text{Me2}})(\text{H}_{\text{eq}}\cdots\text{TFA}_{\text{ax}})(\text{Me}_{\text{eq}})]^{\dagger}$
Cartesian coordinates

Atom	x	y	z
Rh1	-1.65466	0.456131	-2.01686

N2	-2.6094	-0.82123	-0.47747
C3	-3.51788	-1.75881	-0.69809
C4	-3.96555	-2.64449	0.307079
C5	-3.43469	-2.54311	1.57218
C6	-6.64106	1.901654	-1.49924
C7	-6.33769	1.454975	-2.76332
C8	-4.97649	1.274561	-3.11043
N9	-3.97487	1.527069	-2.29102
H10	-3.89838	-1.82383	-1.71348
H11	-4.71327	-3.39315	0.065438
H12	-3.74821	-3.215	2.367244
O13	-1.85209	-1.27009	-3.41572
H14	-4.70743	0.900697	-4.09693
H15	-0.19121	-0.58036	-2.0848
C16	-0.78272	-1.90173	-3.34844
O17	0.219362	-1.59031	-2.61662
C18	-0.59475	-3.16636	-4.20284
F19	-0.1956	-4.19675	-3.4363
F20	-1.73275	-3.51866	-4.81579
F21	0.342104	-2.94994	-5.14285
C22	-4.25125	1.994533	-1.03492
C23	-5.59432	2.18339	-0.58324
C24	-5.82799	2.624196	0.744644
C25	-4.76531	2.870323	1.581957
C26	-3.43638	2.704323	1.124434
C27	-3.15743	2.271429	-0.15887
H28	-6.85182	2.759905	1.084699
H29	-4.93963	3.205968	2.600471
H30	-2.61338	2.927821	1.796784
C31	-2.07484	-0.69001	0.776011
C32	-2.45597	-1.55296	1.844795
C33	-1.82939	-1.40064	3.108183
C34	-0.86699	-0.43309	3.282628
C35	-0.50629	0.426939	2.219227
C36	-1.09686	0.325437	0.970319
H37	-2.11247	-2.06163	3.922833
H38	-0.3803	-0.31745	4.247051
H39	0.239198	1.198121	2.389026
H40	-7.11439	1.231759	-3.48834
H41	-7.67312	2.04005	-1.18558

C42	-1.73406	2.201819	-0.65643
C43	-0.74458	1.281155	-0.13039
C44	0.63877	1.66691	-0.23097
C45	1.058064	2.850904	-0.78547
C46	0.077211	3.771327	-1.29258
C47	-1.25147	3.434582	-1.2216
H48	1.377811	0.977756	0.171065
H49	-1.9958	4.140094	-1.58287
C50	-0.68243	1.475474	-3.53223
H51	-0.53782	0.785573	-4.37432
H52	-1.31067	2.306027	-3.87465
H53	0.290128	1.872379	-3.2265
C54	0.499699	5.091496	-1.89201
H55	1.068009	5.7013	-1.17823
H56	1.14334	4.947831	-2.76862
H57	-0.36996	5.672777	-2.21072
C58	2.529003	3.184268	-0.85958
H59	2.760433	4.122274	-0.33916
H60	3.134863	2.392724	-0.41008
H61	2.861732	3.30957	-1.89755

Table S337. $[\text{Rh}^{\text{I-III}}(\text{bisq}^{\text{Me2}})(\text{H}_{\text{eq}}\cdots\text{TFA}_{\text{ax}})(\text{Me}_{\text{eq}})]^{\dagger}$ thermodynamic values

Temp	298.15	498.15
E _{gas}	-1787.92	-1787.92
E _{solv}	-1787.94	-1787.94
G	-1787.52	-1787.59
ZPE	288.566	288.566
H _{vib}	18.927	50.248
S _{trans}	45.019	47.569
S _{rot}	37.119	38.649
S _{vib}	121.204	200.130
solv	-10.1	-10.1

Table S338. $[\text{Rh}^{\text{I-III}}(\text{bisq}^{\text{Me2}})(\text{H}_{\text{eq}}\cdots\text{TFA}_{\text{eq}})(\text{Me}_{\text{ax}})]^{\dagger}$ Cartesian coordinates

Atom	x	y	z
Rh1	-1.51301	0.283589	-2.02723

N2	-2.42198	-1.12061	0.517693
C3	-3.19572	-2.16657	0.315204
C4	-3.69052	-2.99368	1.35268
C5	-3.33581	-2.70074	2.646898
C6	-6.14821	1.697507	-1.96253
C7	-5.62335	1.158573	-3.11282
C8	-4.25906	0.810099	-3.15377
N9	-3.42784	0.999269	-2.13041
H10	-3.44472	-2.38214	-0.72272
H11	-4.3287	-3.83962	1.116009
H12	-3.6832	-3.31111	3.477385
H13	-3.83211	0.340868	-4.03071
O14	0.535912	-0.46225	-2.01493
C15	1.09839	-0.04988	-3.03641
O16	0.551617	0.69678	-3.93586
C17	2.574113	-0.38206	-3.29524
F18	2.74108	-0.8983	-4.52212
F19	3.309325	0.752327	-3.21456
F20	3.047185	-1.24977	-2.39753
H21	-0.50213	0.812745	-3.52465
C22	-3.91214	1.608254	-0.98694
C23	-5.29602	1.935244	-0.85546
C24	-5.7675	2.476612	0.367524
C25	-4.89139	2.702966	1.40276
C26	-3.51505	2.430235	1.246087
C27	-3.00435	1.895081	0.074539
H28	-6.82479	2.707703	0.466993
H29	-5.24892	3.116157	2.341724
H30	-2.83508	2.66014	2.059248
C31	-2.06384	-0.80338	1.793153
C32	-2.49612	-1.58798	2.910907
C33	-2.07609	-1.24743	4.221576
C34	-1.24613	-0.16888	4.41511
C35	-0.81931	0.609507	3.316109
C36	-1.20945	0.32897	2.014713
H37	-2.41632	-1.85089	5.059727
H38	-0.91864	0.097421	5.416184
H39	-0.17738	1.467213	3.495425
H40	-6.24044	0.97463	-3.98614
H41	-7.20268	1.947778	-1.88604

C42	-1.53174	1.731203	-0.11648
C43	-0.69199	1.160469	0.893912
C44	0.67573	1.407845	0.836864
C45	1.281	2.210383	-0.15079
C46	0.478867	2.769915	-1.14668
C47	-0.91212	2.50219	-1.13884
H48	1.313228	0.941429	1.583381
H49	-1.54328	3.081784	-1.80492
C50	-1.99022	-1.30446	-3.26516
H51	-2.01491	-1.03598	-4.33049
H52	-1.25035	-2.10282	-3.12848
H53	-2.97856	-1.6995	-2.99249
C54	1.060948	3.658253	-2.22018
H55	0.280357	4.038193	-2.88448
H56	1.587466	4.518863	-1.78906
H57	1.785296	3.115245	-2.83801
C58	2.773373	2.445326	-0.11532
H59	3.015261	3.514538	-0.0717
H60	3.226423	1.965327	0.756599
H61	3.264054	2.044072	-1.00945

Table S339. $[\text{Rh}^{\text{I-III}}(\text{bisq}^{\text{Me2}})(\text{H}_{\text{eq}}\cdots\text{TFA}_{\text{eq}})(\text{Me}_{\text{ax}})]^{\ddagger}$
thermodynamic values

Temp	298.15	498.15
E _{gas}	-1787.93	-1787.93
E _{solv}	-1787.95	-1787.95
G	-1787.53	-1787.59
ZPE	289.356	289.356
H _{vib}	18.726	49.940
S _{trans}	45.019	47.569
S _{rot}	37.136	38.666
S _{vib}	119.624	198.274
solv	-8.8	-8.8

Table S340.
 $[\text{Rh}^{\text{III}}(\text{bisq}^{\text{Me2}})(\text{Me}_{\text{ax}}\cdots\text{H}\cdots\text{TFA}_{\text{eq}})(\text{TFA}_{\text{eq}})]^{+\ddagger}$
Cartesian coordinates

Atom	x	y	z
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Rh1	-2.67375	0.330599	-1.42921
N2	-1.44436	-0.76079	-0.01021
C3	-1.6716	-2.07098	0.059788
C4	-0.99498	-2.94751	0.922499
C5	-0.02931	-2.4351	1.751982
C6	-6.11816	-0.29831	1.983591
C7	-6.20018	-1.03667	0.827024
C8	-5.23655	-0.84001	-0.1806
N9	-4.25761	0.050688	-0.08031
H10	-2.42496	-2.46363	-0.60621
H11	-1.24052	-4.00326	0.904938
H12	0.532221	-3.07486	2.426674
H13	-5.26908	-1.43516	-1.08347
O14	-1.04529	0.872958	-2.58643
C15	-0.48559	-0.02305	-3.27538
O16	-0.84197	-1.22084	-3.35275
C17	0.774662	0.448341	-4.03418
F18	1.253613	-0.50083	-4.83149
F19	0.493216	1.538443	-4.76116
F20	1.719666	0.776435	-3.12792
O21	-3.99903	1.339585	-2.61939
C22	-3.88208	1.361795	-3.91781
O23	-3.03808	0.85274	-4.63036
C24	-5.092	2.103093	-4.5526
F25	-4.83428	2.461294	-5.81017
F26	-6.16112	1.280213	-4.54918
F27	-5.42516	3.212027	-3.85617
H28	-2.0808	-1.21255	-2.8533
C29	-3.38263	-1.50632	-2.74635
H30	-3.20261	-1.76257	-3.79859
H31	-3.48335	-2.42517	-2.1677
H32	-4.31672	-0.95468	-2.77646
C33	0.244518	-1.04819	1.727726
C34	-0.49981	-0.20591	0.835653
C35	-0.21595	1.193816	0.827611
C36	0.788587	1.681839	1.651858
C37	1.523538	0.850391	2.518924
C38	1.249679	-0.49406	2.561193
H39	0.998353	2.746952	1.63663
H40	2.295706	1.279157	3.149348

H41	1.799685	-1.15666	3.222784
C42	-4.18369	0.851573	1.040664
C43	-5.09546	0.670978	2.125115
C44	-4.94741	1.464597	3.290831
C45	-3.9452	2.403601	3.365347
C46	-3.08136	2.609097	2.267095
C47	-3.18913	1.861024	1.107322
H48	-5.63841	1.319586	4.115908
H49	-3.82872	3.011575	4.25679
H50	-2.33063	3.39205	2.321651
H51	-6.83022	-0.44236	2.790743
H52	-6.97753	-1.77688	0.675223
C53	-0.92291	2.148409	-0.05271
C54	-2.35792	2.230049	-0.09539
C55	-2.92517	3.216899	-0.96686
C56	-2.16798	4.02577	-1.79931
C57	-0.75441	3.915538	-1.73921
C58	-0.17018	2.990609	-0.86306
H59	-4.00468	3.321746	-0.97227
H60	0.910091	2.882843	-0.86691
C61	-2.83551	4.99428	-2.74433
H62	-2.49215	4.83872	-3.77317
H63	-3.91881	4.869576	-2.73729
H64	-2.60562	6.034372	-2.48436
C65	0.120924	4.728428	-2.64931
H66	-0.20453	5.771188	-2.70899
H67	1.165615	4.703401	-2.33221
H68	0.072571	4.317839	-3.66712

Table S341.

$[\text{Rh}^{\text{III}}(\text{bisq}^{\text{Me2}})(\text{Me}_{\text{ax}}\cdots\text{H}\cdots\text{TFA}_{\text{eq}})(\text{TFA}_{\text{eq}})]^{+\ddagger}$

thermodynamic values

Temp	298.15	498.15
E_{gas}	-2313.88	-2313.88
E_{solv}	-2313.95	-2313.95
G	-2313.51	-2313.58
ZPE	309.410	309.410
H_{vib}	22.941	59.639
S_{trans}	45.540	48.090

S_{rot}	37.784	39.314
S_{vib}	147.913	240.481
solv	-43.6	-43.6

Table S342.

[Rh^{III}(bisq^{Me2})(Me_{eq}...H...TFA_{ax})(TFA_{eq})]⁺⁺

Cartesian coordinates

Atom	x	y	z
Rh1	-1.4402	0.109698	-1.58406
N2	-1.85123	-1.34115	-0.09938
C3	-1.96608	-2.63695	-0.35501
C4	-2.38856	-3.5563	0.62767
C5	-2.71861	-3.0985	1.88308
C6	-6.21875	1.385848	-1.42983
C7	-5.75138	0.2385	-2.01967
C8	-4.37082	-0.01787	-1.99436
N9	-3.47619	0.787732	-1.4224
H10	-1.74351	-2.9529	-1.36699
H11	-2.46417	-4.60625	0.367883
H12	-3.07795	-3.78146	2.647696
H13	-3.97694	-0.90587	-2.47117
O14	0.385635	-0.80986	-1.67121
C15	1.48043	-0.28399	-2.13478
O16	1.668599	0.809475	-2.63639
C17	2.66765	-1.26137	-1.90809
F18	2.903829	-1.36659	-0.57498
F19	2.394882	-2.4907	-2.37562
F20	3.780554	-0.81749	-2.49205
H21	-0.48244	1.893234	-4.03466
H22	-0.80608	0.533245	-3.69312
O23	-1.98988	-1.3593	-2.95318
C24	-1.40878	-1.35622	-4.08106
O25	-0.6994	-0.43334	-4.53029
C26	-1.65809	-2.61541	-4.94054
F27	-0.96244	-2.58129	-6.06983
F28	-1.3124	-3.70442	-4.23565
F29	-2.96929	-2.68748	-5.22713
C30	-1.06707	1.756461	-3.11072
H31	-2.05894	2.171315	-3.29075

H32	-0.48496	2.331158	-2.40166
C33	-5.30944	2.268535	-0.80123
C34	-3.91331	1.938983	-0.78976
C35	-3.00739	2.838848	-0.14297
C36	-3.50655	4.009406	0.415264
C37	-4.87678	4.332821	0.390799
C38	-5.76538	3.4704	-0.20177
H39	-2.81424	4.682566	0.911336
H40	-5.22014	5.254878	0.848342
H41	-6.82773	3.693443	-0.2285
C42	-2.08877	-0.86394	1.162062
C43	-2.57782	-1.72114	2.190002
C44	-2.88432	-1.15686	3.454726
C45	-2.6863	0.187318	3.676161
C46	-2.13532	1.01038	2.666384
C47	-1.82332	0.502394	1.417398
H48	-3.26844	-1.79793	4.242964
H49	-2.92081	0.619689	4.643652
H50	-1.92288	2.0522	2.888068
H51	-7.27632	1.633338	-1.43808
H52	-6.41144	-0.46629	-2.51231
C53	-1.55361	2.583423	-0.04314
C54	-1.04174	1.331027	0.425638
C55	0.382233	1.189124	0.500237
C56	1.268927	2.197159	0.154245
C57	0.733931	3.444058	-0.26512
C58	-0.65447	3.600902	-0.36794
H59	0.774265	0.249794	0.877993
H60	-1.04487	4.540248	-0.74848
C61	1.648086	4.578519	-0.63288
H62	2.326647	4.821154	0.193052
H63	2.280512	4.301042	-1.48494
H64	1.091146	5.479677	-0.8975
C65	2.75824	1.97882	0.236556
H66	3.221764	2.125902	-0.74458
H67	3.229962	2.678837	0.935506
H68	2.991453	0.962776	0.559355

Table S343.[Rh^{III}(bisq^{Me2})(Me_{eq}...H...TFA_{ax})(TFA_{eq})]⁺⁺

thermodynamic values

Temp	298.15	498.15
E _{gas}	-2313.89	-2313.89
E _{solv}	-2313.95	-2313.95
G	-2313.51	-2313.58
ZPE	309.748	309.748
H _{vib}	22.831	59.448
S _{trans}	45.540	48.090
S _{rot}	37.890	39.420
S _{vib}	147.196	239.558
solv	-41.2	-41.2

Table S344.[Rh^{III}(bisq^{Me2})(Me_{eq}...H...TFA_{eq})(TFA_{ax})]⁺⁺

Cartesian coordinates

Atom	x	y	z
Rh1	-2.60982	0.143106	-1.47024
N2	-1.59093	-1.01846	0.010642
C3	-1.98729	-2.27552	0.184942
C4	-1.38128	-3.15099	1.103634
C5	-0.32272	-2.69907	1.851894
C6	-6.02295	0.260027	1.982751
C7	-6.22681	-0.49769	0.852585
C8	-5.27007	-0.46538	-0.18112
N9	-4.18963	0.305088	-0.11887
H10	-2.797	-2.61231	-0.4503
H11	-1.75428	-4.16518	1.189973
H12	0.179807	-3.34743	2.563983
H13	-5.35601	-1.10043	-1.0553
O14	-0.94087	-0.25489	-2.64268
C15	-0.86878	0.364712	-3.74113
O16	-1.68003	1.225345	-4.15212
C17	0.387743	0.08884	-4.59356
F18	1.351309	0.955771	-4.19717
F19	0.83683	-1.15309	-4.41087
F20	0.145615	0.287929	-5.88687

H21	-3.96481	1.953858	-3.76461
H22	-2.72716	1.170751	-3.33598
O23	-3.48359	-1.56713	-2.11057
C24	-3.43205	-2.02912	-3.33849
O25	-2.93945	-1.54374	-4.33097
C26	-4.18252	-3.39065	-3.38025
F27	-4.14757	-3.92923	-4.59276
F28	-3.63032	-4.25655	-2.50248
F29	-5.4734	-3.20925	-3.0207
C30	-4.02702	1.224064	-2.94392
H31	-4.62023	0.387578	-3.30498
H32	-4.53298	1.753167	-2.1417
C33	-3.98118	1.121073	0.968708
C34	-4.88013	1.09314	2.076183
C35	-4.59417	1.896026	3.209354
C36	-3.47448	2.695552	3.225704
C37	-2.62014	2.752657	2.10087
C38	-2.85816	1.986634	0.972833
H39	-5.27306	1.871061	4.056534
H40	-3.2538	3.309264	4.093195
H41	-1.77142	3.430403	2.111796
C42	-0.53352	-0.525	0.744374
C43	0.13647	-1.37052	1.685726
C44	1.251673	-0.87681	2.408786
C45	1.702199	0.403638	2.200381
C46	1.044587	1.233696	1.269886
C47	-0.06305	0.805837	0.552732
H48	1.746579	-1.53447	3.116573
H49	2.560723	0.783378	2.744643
H50	1.405228	2.246418	1.116572
H51	-7.09381	-1.13982	0.74622
H52	-6.72808	0.23024	2.80864
C53	-0.68719	1.762474	-0.39882
C54	-2.03774	2.200408	-0.27321
C55	-2.46389	3.271925	-1.11734
C56	-1.64817	3.870033	-2.06001
C57	-0.30729	3.404588	-2.18772
C58	0.13429	2.372742	-1.36525
H59	-3.47214	3.651779	-0.97655
H60	1.151217	2.010414	-1.47703

C61	-2.16853	4.98631	-2.93034
H62	-1.57579	5.900252	-2.81125
H63	-2.12117	4.712968	-3.99097
H64	-3.20704	5.226296	-2.68981
C65	0.613299	4.000506	-3.2167
H66	0.243391	3.787674	-4.22688
H67	0.668248	5.090267	-3.12005
H68	1.622817	3.594166	-3.1374

Table S345.

$[\text{Rh}^{\text{III}}(\text{bisq}^{\text{Me2}})(\text{Me}_{\text{eq}}\cdots\text{H}\cdots\text{TFA}_{\text{eq}})(\text{TFA}_{\text{ax}})]^{+\ddagger}$

thermodynamic values

Temp	298.15	498.15
E_{gas}	-2313.89	-2313.89
E_{solv}	-2313.96	-2313.96
G	-2313.52	-2313.59
ZPE	309.774	309.774
H_{vib}	22.856	59.468
S_{trans}	45.540	48.090
S_{rot}	37.835	39.365
S_{vib}	147.899	240.248
solv	-41.1	-41.1

Table S346. $[\text{Rh}^{\text{III}}(\text{bisq}^{\text{Me2}})(\text{Me}_{\text{ax}}\cdots\text{TFA}_{\text{eq}})(\text{TFA}_{\text{eq}})]^{\ddagger}$

Cartesian coordinates

Atom	x	y	z
Rh1	-1.71476	0.260964	-1.82819
N2	-2.34643	-0.87182	-0.16195
C3	-3.08933	-1.94503	-0.4105
C4	-3.46398	-2.88624	0.564864
C5	-3.01375	-2.71021	1.849312
C6	-6.39493	1.541631	-1.7661
C7	-5.84366	1.005801	-2.90527
C8	-4.45204	0.787101	-2.95368
N9	-3.62869	1.106589	-1.95808
H10	-3.38734	-2.08678	-1.44309
H11	-4.07228	-3.73797	0.280357
H12	-3.24935	-3.42542	2.6328

H13	-3.99105	0.318707	-3.81646
O14	0.130945	-0.65422	-1.48771
C15	1.039786	-0.87148	-2.37077
O16	0.997564	-0.81052	-3.59388
C17	2.366237	-1.31026	-1.68742
F18	3.355012	-1.50011	-2.5721
F19	2.794888	-0.37979	-0.79519
F20	2.198874	-2.46663	-1.00484
O21	-1.00501	1.37265	-3.43618
C22	-1.27857	0.947787	-4.57466
O23	-1.92234	-0.09026	-4.91273
C24	-0.85354	1.843448	-5.75984
F25	-0.36544	1.117006	-6.77288
F26	-1.93423	2.521194	-6.21136
F27	0.073554	2.743883	-5.39996
C28	-4.1367	1.772634	-0.85861
C29	-5.54819	1.94421	-0.70318
C30	-6.05403	2.523063	0.489078
C31	-5.19104	2.950118	1.469516
C32	-3.79482	2.864457	1.270188
C33	-3.25	2.3044	0.127737
H34	-7.12936	2.629983	0.603909
H35	-5.57517	3.391929	2.384303
H36	-3.12317	3.278831	2.016168
C37	-1.91858	-0.63414	1.129827
C38	-2.22104	-1.58128	2.165449
C39	-1.72299	-1.38952	3.478893
C40	-0.94964	-0.29357	3.768033
C41	-0.68065	0.656889	2.76222
C42	-1.15114	0.531305	1.463371
H43	-1.9614	-2.12715	4.240147
H44	-0.55483	-0.14313	4.768449
H45	-0.09277	1.536229	3.007717
H46	-6.45507	0.716225	-3.7533
H47	-7.46885	1.677965	-1.67002
C48	-1.77797	2.420176	-0.12731
C49	-0.80518	1.618603	0.505214
C50	0.549868	1.898183	0.268925
C51	0.969042	2.912792	-0.59163
C52	-0.00441	3.725122	-1.21114

C53	-1.35026	3.478653	-0.94531
H54	1.294852	1.246716	0.713937
H57	-2.1035	4.103889	-1.41827
C58	-1.95703	-1.69033	-3.79583
H59	-1.59023	-2.1089	-4.72417
H60	-1.32195	-1.89077	-2.94585
H61	-3.02667	-1.78131	-3.65067
C61	0.383154	4.799124	-2.19875
H62	1.217799	5.412256	-1.84224
H63	0.691174	4.346443	-3.14996
H64	-0.45977	5.463059	-2.41104
C64	2.439935	3.103813	-0.87711
H65	2.636225	3.097265	-1.9553
H66	2.809905	4.063102	-0.49192
H67	3.033916	2.303717	-0.43026

Table S347. $[\text{Rh}^{\text{III}}(\text{bisq}^{\text{Me}_2})(\text{Me}_{\text{ax}}\cdots\text{TFA}_{\text{eq}})(\text{TFA}_{\text{eq}})]^{\ddagger}$
thermodynamic values

Temp	298.15	498.15
E_{gas}	-2313.47	-2313.47
E_{solv}	-2313.49	-2313.49
G	-2313.06	-2313.14
ZPE	303.342	303.342
H_{vib}	23.267	59.687
S_{trans}	45.536	48.086
S_{rot}	37.843	39.373
S_{vib}	152.834	244.724
Solv	-16.1	-16.1

Table S348. $[\text{Rh}^{\text{III}}(\text{bisq}^{\text{Me}_2})(\text{Me}_{\text{eq}}\cdots\text{TFA}_{\text{ax}})(\text{TFA}_{\text{eq}})]^{\ddagger}$
Cartesian coordinates

Atom	x	y	z
Rh1	-1.4315	0.755151	-2.25473
N2	-2.18036	-1.02944	-0.08125
C3	-2.81075	-2.11975	-0.4685
C4	-3.23943	-3.13374	0.421948
C5	-2.97152	-2.98592	1.760966
C6	-6.19217	1.729379	-2.0457

C7	-5.64523	1.334221	-3.24344
C8	-4.25331	1.129079	-3.33807
N9	-3.42763	1.308154	-2.31067
H10	-2.97836	-2.21732	-1.53948
H11	-3.75939	-4.0066	0.039251
H12	-3.27542	-3.74165	2.481611
O13	-1.78449	-0.95832	-3.43394
H14	-3.79972	0.81756	-4.27076
O15	0.499413	0.086698	-1.95101
C16	1.288234	-0.38871	-2.84175
O17	1.214647	-0.37294	-4.06879
C18	2.52686	-1.05391	-2.17823
F19	3.350448	-1.60128	-3.08272
F20	3.244392	-0.13633	-1.47821
F21	2.163384	-2.02144	-1.31176
C22	-1.91018	-0.79577	-4.66644
O23	-1.86221	0.270522	-5.33568
C24	-2.27976	-2.05039	-5.49274
F25	-1.54471	-2.13101	-6.60808
F26	-2.11868	-3.18071	-4.79376
F27	-3.5827	-1.96549	-5.85004
C28	-3.94214	1.757697	-1.1124
C29	-5.34245	1.957838	-0.93447
C30	-5.8206	2.360925	0.338288
C31	-4.93629	2.569099	1.371742
C32	-3.54711	2.404499	1.173662
C33	-3.03475	2.004834	-0.04849
H34	-6.88908	2.498907	0.479858
H35	-5.30106	2.87626	2.347649
H36	-2.86535	2.602387	1.994084
C37	-1.89602	-0.86079	1.24047
C38	-2.27335	-1.83751	2.216427
C39	-1.93329	-1.64466	3.579376
C40	-1.2243	-0.52995	3.959702
C41	-0.84182	0.433909	2.999934
C42	-1.16522	0.303806	1.657633
H43	-2.23421	-2.39227	4.308845
H44	-0.95618	-0.38142	5.001911
H45	-0.28606	1.310019	3.322207
H46	-6.2612	1.16221	-4.11964

H47	-7.26374	1.873421	-1.93647
C48	-1.56198	1.92082	-0.29256
C49	-0.68985	1.310414	0.673985
C50	0.651194	1.649221	0.655324
C51	1.215508	2.572645	-0.25566
C52	0.393163	3.172521	-1.20271
C53	-0.98907	2.830925	-1.23366
H54	1.31724	1.149768	1.35371
H57	-1.65951	3.482193	-1.78868
C58	-0.77342	1.882437	-4.70402
H59	0.153412	1.321212	-4.6453
H60	-1.1199	2.18301	-5.68354
H61	-1.01012	2.568963	-3.90378
C61	0.927343	4.159081	-2.2099
H62	0.11659	4.676595	-2.7311
H63	1.562875	4.919302	-1.74267
H64	1.541834	3.654315	-2.96777
C64	2.700088	2.842154	-0.20381
H65	2.927605	3.913786	-0.22518
H66	3.143205	2.422128	0.703204
H67	3.207807	2.378798	-1.05747

Table S349. $[\text{Rh}^{\text{III}}\text{I}(\text{bisq}^{\text{Me2}})(\text{Me}_{\text{eq}}\cdots\text{TFA}_{\text{ax}})(\text{TFA}_{\text{eq}})]^{\dagger}$
thermodynamic values

Temp	298.15	498.15
E _{gas}	-2313.46	-2313.46
E _{solv}	-2313.49	-2313.49
G	-2313.06	-2313.13
ZPE	302.880	302.880
H _{vib}	23.443	59.894
S _{trans}	45.536	48.086
S _{rot}	37.936	39.466
S _{vib}	153.772	245.741
solv	-14.7	-14.7

Table S350. $[\text{Rh}^{\text{III}}\text{I}(\text{bisq}^{\text{Me2}})(\text{Me}_{\text{eq}}\cdots\text{TFA}_{\text{eq}})(\text{TFA}_{\text{ax}})]^{\dagger}$
Cartesian coordinates

Atom	x	y	z
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Rh1	-1.38978	0.730435	-2.13541
N2	-2.15955	-0.93847	-0.04458
C3	-2.80277	-2.01792	-0.446
C4	-3.23647	-3.03882	0.433342
C5	-2.96285	-2.91255	1.77278
C6	-6.11008	1.820685	-1.97787
C7	-5.57831	1.306214	-3.13757
C8	-4.19243	1.055819	-3.21555
N9	-3.3641	1.328624	-2.21423
H10	-2.9699	-2.09961	-1.51719
H11	-3.76361	-3.90165	0.038503
H12	-3.27061	-3.67541	2.484079
O13	-2.03015	-0.84889	-3.36714
H14	-3.7474	0.579554	-4.08137
O15	0.5163	-0.05804	-1.94847
C16	1.39276	0.353956	-2.73876
O17	1.31782	1.243759	-3.62668
C18	2.790504	-0.29788	-2.60685
F19	3.082654	-1.00299	-3.70771
F20	3.737552	0.660029	-2.46282
F21	2.869174	-1.11094	-1.54648
C22	-1.34951	-1.59507	-4.1661
O23	-0.21415	-1.46503	-4.60362
C24	-2.21054	-2.80123	-4.6385
F25	-1.53668	-3.62421	-5.44927
F26	-2.65405	-3.53277	-3.58655
F27	-3.30492	-2.36452	-5.30887
C28	-3.86257	1.863496	-1.04884
C29	-5.25637	2.103957	-0.88167
C30	-5.71912	2.577318	0.372563
C31	-4.82674	2.794083	1.397688
C32	-3.44259	2.574048	1.210797
C33	-2.9437	2.119256	0.002874
H34	-6.78253	2.751325	0.511592
H35	-5.18145	3.146088	2.36203
H36	-2.7562	2.770206	2.028157
C37	-1.86658	-0.79077	1.279277
C38	-2.25171	-1.77786	2.241999
C39	-1.90542	-1.6114	3.606792
C40	-1.18312	-0.51127	4.003043

C41	-0.79053	0.461044	3.05662
C42	-1.11597	0.355971	1.71286
H43	-2.21283	-2.36774	4.324803
H44	-0.91073	-0.38133	5.046505
H45	-0.22346	1.325149	3.391376
H46	-6.20476	1.066692	-3.99006
H47	-7.17755	2.000528	-1.88264
C48	-1.47542	1.96862	-0.24648
C49	-0.61834	1.362836	0.741403
C50	0.721932	1.70228	0.742937
C51	1.299406	2.625126	-0.16576
C52	0.502822	3.188636	-1.15541
C53	-0.87686	2.836012	-1.21183
H54	1.375946	1.213388	1.460383
H57	-1.52985	3.468666	-1.80671
C58	-0.41476	1.715312	-4.53387
H59	-0.45688	0.748922	-5.01792
H60	-1.33775	2.121244	-4.14352
H61	0.255413	2.447097	-4.96311
C62	1.057803	4.179323	-2.14872
H63	0.267749	4.583725	-2.78777
H64	1.549305	5.022086	-1.64816
H65	1.801237	3.703511	-2.79729
C65	2.771226	2.949215	-0.05512
H66	2.950625	4.030403	-0.03791
H67	3.199972	2.524745	0.85693
H68	3.331217	2.542069	-0.90464

Table S351. $[\text{Rh}^{\text{III}}\text{-I}(\text{bisq}^{\text{Me2}})(\text{Me}_{\text{eq}}\cdots\text{TFA}_{\text{eq}})(\text{TFA}_{\text{ax}})]^{\ddagger}$
thermodynamic values

Temp	298.15	498.15
E _{gas}	-2313.47	-2313.47
E _{solv}	-2313.49	-2313.49
G	-2313.06	-2313.13
ZPE	303.170	303.170
H _{vib}	23.264	59.715
S _{trans}	45.536	48.086
S _{rot}	37.919	39.449
S _{vib}	151.506	243.475

solv	-13.9	-13.9
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Table S352. $[\text{Rh}^{\text{III}}\text{-I}(\text{bisq}^{\text{Me2}})(\text{Me}_{\text{ax}}\cdots\text{TFA})(\text{TFA})_2]^{-\ddagger}$
Cartesian coordinates

Atom	x	y	z
Rh1	-1.49519	0.393129	-1.98059
N2	-2.2769	-0.82114	-0.4406
C3	-3.04938	-1.86122	-0.74624
C4	-3.40291	-2.86998	0.171717
C5	-2.91168	-2.80414	1.449637
C6	-6.19431	1.438593	-2.37801
C7	-5.45663	1.173037	-3.50698
C8	-4.05398	1.058594	-3.4062
N9	-3.39826	1.229366	-2.25878
H10	-3.38009	-1.96421	-1.77224
H11	-4.01674	-3.69263	-0.1787
H12	-3.11675	-3.58413	2.179107
H13	-3.43263	0.811035	-4.26347
O14	0.338256	-0.48343	-1.49901
C15	1.303672	-0.70713	-2.31424
O16	1.351771	-0.72921	-3.53659
C17	2.608933	-1.0115	-1.51829
F18	3.66231	-1.24516	-2.32071
F19	2.955982	0.027323	-0.70726
F20	2.467598	-2.09637	-0.71792
O21	-0.52973	1.68192	-3.28394
C22	-0.74271	1.848514	-4.52575
O23	-1.5792	1.35246	-5.28502
C24	0.195827	2.934533	-5.12712
F25	0.493188	2.696272	-6.41691
F26	-0.42356	4.150943	-5.08039
F27	1.363351	3.076966	-4.46303
C28	-4.09573	1.681853	-1.15322
C29	-5.52446	1.713411	-1.15851
C30	-6.21822	2.044485	0.034687
C31	-5.52211	2.389281	1.168707
C32	-4.11192	2.478383	1.133191
C33	-3.38903	2.153073	-0.0008
H34	-7.30556	2.033182	0.02685

H35	-6.05269	2.641334	2.083124
H36	-3.57571	2.847187	2.00298
C37	-1.85092	-0.66965	0.867196
C38	-2.11861	-1.69437	1.833992
C39	-1.59641	-1.59223	3.147862
C40	-0.85047	-0.4985	3.510598
C41	-0.64379	0.541941	2.583204
C42	-1.1335	0.498701	1.285339
H43	-1.79984	-2.39489	3.852489
H44	-0.43894	-0.41586	4.512977
H45	-0.09791	1.428734	2.89132
H46	-5.92922	0.998933	-4.46809
H47	-7.28101	1.464408	-2.40468
C48	-1.93285	2.486562	-0.09503
C49	-0.89148	1.701371	0.437284
C50	0.431346	2.135695	0.253754
C51	0.75168	3.286271	-0.46461
C52	-0.29236	4.096735	-0.9531
C53	-1.60804	3.687091	-0.7419
H54	1.233377	1.492228	0.598277
H57	-2.41793	4.29489	-1.1392
C58	-1.78422	-1.51518	-3.67878
H59	-1.12908	-1.02653	-4.38192
H60	-1.34851	-2.10901	-2.89305
H61	-2.82181	-1.24069	-3.63182
O62	-2.14121	-3.00644	-4.77639
C63	-3.1759	-3.6479	-4.39054
O64	-3.92999	-3.45463	-3.43307
C65	-3.53564	-4.8573	-5.30235
F66	-2.65682	-5.07668	-6.29566
F67	-3.61216	-5.99446	-4.57236
F68	-4.74983	-4.66778	-5.87171
C68	2.193263	3.610032	-0.77515
H69	2.340784	3.661494	-1.86027
H70	2.505055	4.576979	-0.35761
H71	2.860385	2.835618	-0.38896
C71	-0.00826	5.342545	-1.75745
H72	-0.91605	5.939012	-1.89106
H73	0.748784	5.978864	-1.28351
H74	0.361759	5.080145	-2.7554

Table S353. $[\text{Rh}^{\text{III-I}}(\text{bisq}^{\text{Me2}})(\text{Me}_{\text{ax}}\cdots\text{TFA})(\text{TFA})_2]^+$ thermodynamic values

Temp	298.15	498.15
E _{gas}	-2839.78	-2839.78
E _{solv}	-2839.85	-2839.85
G	-2839.40	-2839.49
ZPE	321.133	321.133
H _{vib}	27.519	69.178
S _{trans}	45.979	48.529
S _{rot}	38.993	40.523
S _{vib}	187.929	294.127
solv	-46.5	-46.5

Table S354. $[\text{Rh}^{\text{III-I}}(\text{bisq}^{\text{Me2}})(\text{Me}_{\text{ax}}\cdots\text{TFAH})(\text{TFA})_2]^{\ddagger}$ Cartesian coordinates

Atom	x	y	z
Rh1	-1.90551	0.208126	-1.78301
N2	-2.55068	-0.81026	-0.04396
C3	-3.43851	-1.79231	-0.17676
C4	-3.76663	-2.70473	0.841375
C5	-3.11527	-2.60346	2.044422
C6	-6.49144	1.647758	-1.66414
C7	-5.93209	1.241084	-2.85163
C8	-4.54369	1.001294	-2.91233
N9	-3.73505	1.188549	-1.87038
H10	-3.90013	-1.88891	-1.15002
H11	-4.49633	-3.4823	0.644196
H12	-3.29937	-3.31089	2.848336
H13	-4.06641	0.652184	-3.82231
O14	0.02594	-0.85706	-1.6536
C15	0.975758	-1.15225	-2.3755
O16	1.016293	-1.57343	-3.59462
C17	2.395851	-1.11802	-1.75322
F18	3.354373	-0.99642	-2.67441
F19	2.515968	-0.1016	-0.88313
F20	2.59363	-2.26806	-1.07758
O21	-0.96999	1.273695	-3.28796

C22	-1.35678	1.504302	-4.48473
O23	-2.33038	1.069929	-5.10177
C24	-0.43983	2.529902	-5.20845
F25	-0.385	2.303269	-6.52819
F26	-0.93299	3.781619	-5.02529
F27	0.824497	2.531001	-4.73597
C28	-4.24125	1.77229	-0.72376
C29	-5.65095	1.936153	-0.55955
C30	-6.15631	2.411583	0.678175
C31	-5.29356	2.76405	1.688189
C32	-3.89718	2.717405	1.474054
C33	-3.35519	2.249359	0.29015
H34	-7.23156	2.507938	0.80172
H35	-5.6781	3.129852	2.635673
H36	-3.22649	3.097711	2.239089
C37	-1.95711	-0.61167	1.192874
C38	-2.19123	-1.55179	2.252573
C39	-1.51178	-1.42262	3.489974
C40	-0.64321	-0.37992	3.692021
C41	-0.46543	0.583613	2.67985
C42	-1.10342	0.512325	1.448481
H43	-1.69731	-2.15989	4.265962
H44	-0.11345	-0.27383	4.633955
H45	0.1767	1.437992	2.87059
H46	-6.53487	1.060582	-3.73503
H47	-7.5654	1.780056	-1.56281
C48	-1.90125	2.445936	-0.00572
C49	-0.86473	1.639508	0.5029
C50	0.461217	1.990359	0.198065
C51	0.788313	3.072813	-0.61714
C52	-0.25035	3.890455	-1.10945
C53	-1.56548	3.567553	-0.77873
H54	1.257395	1.356001	0.57184
H57	-2.36971	4.195936	-1.15359
C58	-2.56019	-1.63223	-3.39575
H59	-2.2117	-0.9047	-4.11097
H60	-1.88496	-2.20858	-2.78525
H61	-3.60955	-1.62748	-3.14473
O62	-2.79941	-2.9661	-4.66568
C63	-1.72416	-3.1738	-5.31038

O64	-0.59102	-2.70054	-5.1251
C65	-1.86536	-4.20347	-6.46308
F66	-3.12102	-4.26663	-6.93095
F67	-1.05082	-3.90287	-7.48337
F68	-1.5289	-5.42872	-6.00404
H69	0.167975	-1.88557	-4.08797
C69	0.039152	5.069133	-2.00605
H70	-0.85894	5.671657	-2.1666
H71	0.814803	5.72116	-1.58844
H72	0.388799	4.733014	-2.98856
C72	2.225695	3.338951	-0.99523
H73	2.346801	3.322235	-2.08502
H74	2.565071	4.32446	-0.65231
H75	2.893732	2.58388	-0.57453

Table S355. $[\text{Rh}^{\text{III}}\text{-I}(\text{bisq}^{\text{Me2}})(\text{Me}_{\text{ax}}\cdots\text{TFAH})(\text{TFA})_2]^{\dagger}$ thermodynamic values

Temp	298.15	498.15
E_{gas}	-2840.26	-2840.26
E_{solv}	-2840.29	-2840.29
G	-2839.83	-2839.92
ZPE	329.226	329.226
H_{vib}	27.375	69.152
S_{trans}	45.983	48.533
S_{rot}	38.965	40.495
S_{vib}	185.650	292.127
solv	-17.6	-17.6

Table S356. $[\text{Rh}^{\text{III}}\text{-I}(\text{bisq}^{\text{Me2}})(\text{Me}_{\text{ax}}\cdots\text{TFA})(\text{TFA}_{\text{eq}})(\text{TFAH}_{\text{eq}})]^{\dagger}$ Cartesian coordinates

Atom	x	y	z
Rh1	-1.07649	0.687951	-1.76473
N2	-1.65434	-0.8914	-0.5278
C3	-1.86821	-2.09974	-1.04205
C4	-2.54753	-3.12107	-0.34662
C5	-3.04899	-2.85577	0.902673
C6	-5.51832	2.737453	-1.48669

C7	-5.27615	1.583082	-2.18512
C8	-3.97913	1.042213	-2.15843
N9	-2.96402	1.566326	-1.47678
H10	-1.54898	-2.28505	-2.06172
H11	-2.69574	-4.07282	-0.84414
H12	-3.6277	-3.59714	1.447345
H13	-3.76412	0.156483	-2.73876
O14	0.742063	-0.43478	-1.96438
C15	1.959825	-0.2567	-2.08554
O16	2.600149	0.80613	-2.39114
C17	2.89399	-1.46357	-1.83656
F18	3.645154	-1.70576	-2.9208
F19	3.717739	-1.19093	-0.8034
F20	2.200521	-2.56634	-1.54008
O21	-0.7659	2.368524	-3.01668
C22	0.247738	3.034322	-3.33304
O23	1.468764	2.789254	-3.18187
C24	-0.04392	4.41824	-3.96671
F25	0.145824	5.376792	-3.02505
F26	0.784216	4.675707	-4.98803
F27	-1.30457	4.523423	-4.40831
H28	1.98224	1.665577	-2.69642
C29	-3.18647	2.697701	-0.71048
C30	-4.47708	3.327563	-0.73243
C31	-4.7045	4.526154	-0.01069
C32	-3.69329	5.091808	0.723441
C33	-2.43769	4.455711	0.779307
C34	-2.15866	3.276365	0.102358
H35	-5.68984	4.981276	-0.05626
H36	-3.8549	6.013605	1.273944
H37	-1.65213	4.889636	1.3904
C38	-2.02298	-0.63753	0.780601
C39	-2.79666	-1.59727	1.506348
C40	-3.26713	-1.28135	2.806075
C41	-2.94919	-0.0761	3.384203
C42	-2.10198	0.82576	2.705274
C43	-1.61965	0.568394	1.432691
H44	-3.86869	-2.01503	3.335701
H45	-3.30764	0.169511	4.37935
H46	-1.78176	1.735075	3.205491

H47	-6.04251	1.090639	-2.77317
H48	-6.49577	3.211781	-1.49887
C49	-0.7905	2.71366	0.285778
C50	-0.54658	1.462902	0.885997
C51	0.784088	1.099657	1.15896
C52	1.872774	1.90958	0.833823
C53	1.627317	3.154959	0.214124
C54	0.307701	3.532096	-0.02996
H55	0.96702	0.146805	1.649639
H58	0.117172	4.483009	-0.51959
C59	-1.59031	-0.40968	-3.85656
H60	-1.82243	0.5093	-4.37261
H61	-0.58229	-0.78853	-3.87213
H62	-2.35687	-0.99126	-3.37977
O63	-1.9584	-1.44786	-5.50531
C64	-2.17432	-2.66627	-5.1892
O65	-2.20211	-3.20081	-4.0749
C66	-2.44625	-3.59935	-6.4043
F67	-2.43924	-2.95805	-7.58471
F68	-1.51442	-4.57426	-6.46055
F69	-3.65142	-4.19491	-6.26975
C69	2.763692	4.056553	-0.2019
H70	2.390866	4.967962	-0.67523
H71	3.3882	4.344417	0.652697
H72	3.417882	3.554324	-0.92366
C72	3.281165	1.451979	1.128577
H73	3.84829	1.301878	0.203088
H74	3.82893	2.189931	1.72637
H75	3.284309	0.504994	1.674462

Table S357. [Rh^{III}]-
[†](bisq^{Me2})(Me_{ax}...TFA)(TFA_{eq})(TFAH_{eq})[‡]
thermodynamic values

Temp	298.15	498.15
E _{gas}	-2840.28	-2840.28
E _{solv}	-2840.31	-2840.31
G	-2839.85	-2839.93
ZPE	328.636	328.636
H _{vib}	27.929	70.023

S_{trans}	45.983	48.533
S_{rot}	39.043	40.573
S_{vib}	185.619	291.883
solv	-19.8	-19.8

Table S358. [Rh^{III}-(bisq^{Me2})(Me_{eq}...TFA)(TFA)₂]⁺
Cartesian coordinates

Atom	x	y	z
Rh1	-1.17748	0.285849	-2.33383
N2	-2.29348	-1.16491	0.400622
C3	-3.00672	-2.26474	0.255047
C4	-3.46813	-3.04101	1.349191
C5	-3.15701	-2.64025	2.62424
C6	-5.90946	1.213528	-2.63324
C7	-5.25059	0.692587	-3.72092
C8	-3.85771	0.489852	-3.65539
N9	-3.14005	0.797617	-2.58161
H10	-3.2186	-2.55345	-0.7725
H11	-4.05254	-3.93756	1.163555
H12	-3.4867	-3.20839	3.491946
O13	-1.32545	-1.31022	-3.69396
H14	-3.31368	0.047725	-4.48109
O15	0.66575	-0.51377	-1.83496
C16	1.830342	-0.22635	-2.2684
O17	2.216306	0.631412	-3.062
C18	2.910877	-1.10398	-1.57115
F19	4.090621	-1.07033	-2.21842
F20	3.138531	-0.63953	-0.31063
F21	2.549697	-2.39684	-1.45648
C22	-2.15258	-2.28338	-3.64445
O23	-3.05829	-2.54097	-2.85397
C24	-1.98924	-3.21511	-4.87942
F25	-2.61237	-4.39678	-4.70727
F26	-2.54954	-2.62225	-5.96771
F27	-0.70463	-3.47627	-5.1799
C28	-3.76374	1.361222	-1.48975
C29	-5.17401	1.563715	-1.47259
C30	-5.77584	2.090055	-0.30177
C31	-4.99839	2.410315	0.7868

C32	-3.59629	2.239748	0.746595
C33	-2.96241	1.720485	-0.36954
H34	-6.85311	2.231161	-0.28218
H35	-5.4584	2.812799	1.685391
H36	-3.00053	2.527527	1.606508
C37	-1.97086	-0.7461	1.654079
C38	-2.3828	-1.46737	2.820849
C39	-2.00675	-1.00916	4.107931
C40	-1.2371	0.123217	4.233543
C41	-0.82627	0.837091	3.086718
C42	-1.17204	0.43811	1.801743
H43	-2.33245	-1.56642	4.983222
H44	-0.94501	0.481104	5.217453
H45	-0.23196	1.737885	3.209877
H46	-5.7792	0.416092	-4.62692
H47	-6.9863	1.361578	-2.64566
C48	-1.47237	1.63885	-0.46782
C49	-0.65891	1.20732	0.63802
C50	0.685374	1.554453	0.631996
C51	1.290358	2.354941	-0.36044
C52	0.513156	2.827948	-1.41386
C53	-0.85462	2.444076	-1.47571
H54	1.316304	1.168265	1.427968
H57	-1.49298	3.000748	-2.15432
C58	-0.63443	1.402341	-4.42233
H59	-0.96628	0.544659	-4.98643
H60	-1.30222	2.221615	-4.2223
H61	0.4043	1.440719	-4.12632
O62	-0.18891	2.326869	-6.17559
C63	-0.49863	3.55841	-6.14055
O64	-1.01138	4.24172	-5.24504
C65	-0.172	4.326747	-7.45792
F66	0.351575	3.554713	-8.4294
F67	-1.28987	4.901121	-7.96517
F68	0.712198	5.324851	-7.22062
C68	2.767973	2.65328	-0.28394
H69	2.967691	3.732104	-0.28953
H70	3.21157	2.228633	0.620911
H71	3.283652	2.22158	-1.14906
C71	1.084359	3.734648	-2.47212

H72	0.324224	4.069448	-3.18211
H73	1.557822	4.617486	-2.023
H74	1.857696	3.199428	-3.03499

Table S359. $[\text{Rh}^{\text{III}}\text{-(bisq}^{\text{Me2}})(\text{Me}_{\text{eq}}\cdots\text{TFA})(\text{TFA})_2]^{+}$
thermodynamic values

Temp	298.15	498.15
E_{gas}	-2839.78	-2839.78
E_{solv}	-2839.85	-2839.85
G	-2839.40	-2839.49
ZPE	321.023	321.023
H_{vib}	26.883	68.152
S_{trans}	45.979	48.529
S_{rot}	39.151	40.681
S_{vib}	186.109	292.325
solv	-46.2	-46.2

Table S360. $[\text{Rh}^{\text{III}}\text{-(bisq}^{\text{Me2}})(\text{Me}_{\text{eq}}\cdots\text{TFAH})(\text{TFA})_2]^{+}$
(TFAH H-bonded to TFA_{ax}) Cartesian coordinates

Atom	x	y	z
Rh1	-1.62039	1.000469	-2.20921
N2	-2.47824	-0.77199	-0.2491
C3	-3.28091	-1.72354	-0.68179
C4	-3.72208	-2.80567	0.115586
C5	-3.28711	-2.88175	1.415178
C6	-6.3329	1.975089	-1.68042
C7	-5.86738	1.559011	-2.90673
C8	-4.48561	1.342761	-3.08684
N9	-3.59956	1.540956	-2.11734
H10	-3.58468	-1.6545	-1.72126
H11	-4.37772	-3.55858	-0.31017
H12	-3.58805	-3.70164	2.063174
O13	-2.15406	-0.55357	-3.75755
H14	-4.09186	0.971356	-4.02597
O15	0.387623	0.459929	-2.26123
C16	0.769519	-0.76745	-2.20473
O17	0.115936	-1.80172	-2.29635
C18	2.298148	-0.87422	-1.94526

F19	2.76979	-2.09397	-2.22539
F20	3.000991	0.021581	-2.6725
F21	2.563134	-0.62094	-0.63743
C22	-1.46319	-1.39288	-4.34914
O23	-0.50834	-1.20212	-5.19375
C24	-1.85219	-2.88887	-4.27749
F25	-0.81091	-3.69881	-4.44668
F26	-2.45886	-3.19191	-3.12367
F27	-2.73912	-3.11962	-5.2773
C28	-4.03323	1.981467	-0.88696
C29	-5.41616	2.192924	-0.62123
C30	-5.8055	2.5746	0.688559
C31	-4.85414	2.733159	1.670478
C32	-3.48201	2.538357	1.387251
C33	-3.05624	2.169731	0.124112
H34	-6.8598	2.725933	0.902974
H35	-5.15271	3.016022	2.67574
H36	-2.74869	2.680128	2.174922
C37	-2.046	-0.81472	1.044747
C38	-2.42458	-1.87819	1.925542
C39	-1.94035	-1.90596	3.257738
C40	-1.10078	-0.91368	3.70534
C41	-0.72536	0.139694	2.843943
C42	-1.17633	0.217473	1.534472
H43	-2.24361	-2.71983	3.911721
H44	-0.7272	-0.92941	4.725248
H45	-0.07358	0.923053	3.220376
H46	-6.54176	1.377119	-3.73653
H47	-7.39455	2.129748	-1.50748
C48	-1.60631	2.027807	-0.22197
C49	-0.70749	1.305071	0.645217
C50	0.639795	1.602037	0.586058
C51	1.19199	2.584919	-0.2744
C52	0.351211	3.290738	-1.12542
C53	-1.0424	2.991021	-1.11625
H54	1.324052	1.014903	1.191484
H57	-1.71561	3.700478	-1.58896
C58	-1.03433	2.309129	-4.20305
H59	-0.04995	1.963163	-3.93637
H60	-1.72841	1.649706	-4.69558

H61	-1.3702	3.286224	-3.89789
O62	-0.37943	3.01264	-5.87167
C63	0.187254	2.107462	-6.55514
O64	0.231679	0.879263	-6.36821
C65	0.994858	2.636802	-7.77131
F66	0.545532	3.826973	-8.19986
F67	2.287293	2.78443	-7.41009
F68	0.945245	1.77623	-8.79903
H69	-0.29253	-0.241	-5.4858
C69	2.68942	2.771098	-0.2909
H70	2.978706	3.825528	-0.34111
H71	3.150711	2.334062	0.598918
H72	3.12197	2.267293	-1.16396
C72	0.872882	4.339671	-2.07411
H73	0.059277	4.928635	-2.50602
H74	1.560847	5.03269	-1.57835
H75	1.425343	3.882515	-2.90519

Table S361. $[\text{Rh}^{\text{III}}\text{I}(\text{bisq}^{\text{Me}_2})(\text{Me}_{\text{eq}}\cdots\text{TFAH})(\text{TFA})_2]^+$
(TFAH H-bonded to TFA_{ax}) thermodynamic values

Temp	298.15	498.15
E_{gas}	-2840.27	-2840.27
E_{solv}	-2840.29	-2840.29
G	-2839.83	-2839.92
ZPE	328.871	328.871
H_{vib}	27.965	70.209
S_{trans}	45.983	48.533
S_{rot}	38.892	40.422
S_{vib}	185.917	292.580
solv	-17.3	-17.3

Table S362. $[\text{Rh}^{\text{III}}\text{I}(\text{bisq}^{\text{Me}_2})(\text{Me}_{\text{eq}}\cdots\text{TFAH})(\text{TFA})_2]^+$
(TFAH H-bonded to TFA_{eq}) Cartesian coordinates

Atom	x	y	z
Rh1	-1.51458	0.984996	-1.8422
N2	-2.17635	-0.93237	0.200153
C3	-2.73084	-2.03902	-0.2548

C4	-3.16464	-3.09535	0.583127
C5	-2.98788	-2.9749	1.939871
C6	-6.26388	1.785027	-1.75816
C7	-5.67259	1.3406	-2.91772
C8	-4.27488	1.161514	-2.96207
N9	-3.49048	1.434444	-1.92413
H10	-2.82552	-2.11396	-1.33608
H11	-3.61633	-3.98043	0.145858
H12	-3.2984	-3.76513	2.619476
O13	-1.97977	-0.60502	-3.13685
H14	-3.78327	0.746873	-3.83353
O15	0.466119	0.162359	-1.68049
C16	1.37346	0.407258	-2.48181
O17	1.562044	1.541237	-3.05874
C18	2.477916	-0.65423	-2.67557
F19	2.942689	-0.6376	-3.931
F20	3.503099	-0.34835	-1.84389
F21	2.054743	-1.88356	-2.37926
C22	-1.20689	-1.17183	-3.99087
O23	-0.09404	-0.83822	-4.39406
C24	-1.88097	-2.43449	-4.5946
F25	-1.07223	-3.09213	-5.4309
F26	-2.26303	-3.29557	-3.62223
F27	-2.99455	-2.08216	-5.27962
C28	-4.05011	1.895074	-0.75276
C29	-5.45839	2.063856	-0.62506
C30	-5.98253	2.469269	0.628703
C31	-5.1356	2.68892	1.691247
C32	-3.73782	2.53748	1.54453
C33	-3.18014	2.150563	0.33875
H34	-7.05681	2.590617	0.736282
H35	-5.5379	2.990077	2.654044
H36	-3.08808	2.733698	2.391191
C37	-1.98562	-0.78981	1.542284
C38	-2.37457	-1.80925	2.468071
C39	-2.12177	-1.64008	3.853224
C40	-1.48476	-0.50793	4.303208
C41	-1.08938	0.498026	3.392743
C42	-1.33265	0.390972	2.032406
H43	-2.42873	-2.4208	4.545143

H44	-1.28191	-0.37911	5.36259
H45	-0.58725	1.385616	3.767523
H46	-6.25914	1.106304	-3.79948
H47	-7.3408	1.913356	-1.69166
C48	-1.70035	2.074488	0.129809
C49	-0.84308	1.436439	1.096294
C50	0.493842	1.787302	1.121141
C51	1.067133	2.758381	0.263048
C52	0.262165	3.389354	-0.67758
C53	-1.11315	3.020499	-0.76779
H54	1.1471	1.27096	1.819898
H57	-1.77445	3.680902	-1.32204
C58	-1.00037	2.25663	-4.05793
H59	-0.69465	1.25295	-4.30151
H60	-2.0149	2.570569	-4.25615
H61	-0.37466	2.874916	-3.44367
O62	-0.35673	2.958048	-5.69428
C63	0.831264	2.683381	-6.02448
O64	1.737994	2.081716	-5.40357
C65	1.260702	3.209721	-7.42061
F66	0.213115	3.590663	-8.16287
F67	2.070883	4.276112	-7.25841
F68	1.937075	2.268391	-8.0941
H69	1.691845	1.671464	-4.14444
C69	2.543209	3.05853	0.368723
H70	2.738071	4.132787	0.462434
H71	2.987507	2.560252	1.234628
H72	3.077752	2.713349	-0.52524
C72	0.80648	4.4642	-1.58473
H73	0.012324	4.932484	-2.17316
H74	1.308852	5.255096	-1.0156
H75	1.544946	4.04956	-2.28053

Table S363. $[\text{Rh}^{\text{III}}(\text{bisq}^{\text{Me2}})(\text{Me}_{\text{eq}}\cdots\text{TFAH})(\text{TFA})_2]^+$ (TFAH H-bonded to TFA_{eq}) thermodynamic values

Temp	298.15	498.15
E_{gas}	-2840.26	-2840.26
E_{solv}	-2840.28	-2840.28

G	-2839.82	-2839.91
ZPE	327.773	327.773
H_{vib}	27.809	70.036
S_{trans}	45.983	48.533
S_{rot}	38.974	40.504
S_{vib}	184.422	291.028
solv	-13.6	-13.6

Table S364. $[\text{Rh}^{\text{III}}(\text{bisq}^{\text{Me2}})(\text{Me}_{\text{eq}}\cdots\text{TFA})(\text{TFA}_{\text{ax}})(\text{TFAH}_{\text{eq}})]^+$ Cartesian coordinates

Atom	x	y	z
Rh1	-1.58506	0.594181	-2.13995
N2	-2.215	-1.01895	0.051898
C3	-2.88497	-2.10961	-0.27247
C4	-3.26342	-3.1062	0.65799
C5	-2.90426	-2.94656	1.973325
C6	-6.304	1.526953	-1.89324
C7	-5.77015	1.061241	-3.07201
C8	-4.379	0.855419	-3.17103
N9	-3.54865	1.124121	-2.16906
H10	-3.13279	-2.22177	-1.32498
H11	-3.81645	-3.97715	0.320607
H12	-3.16233	-3.69197	2.721874
O13	-2.288	-1.08758	-3.23478
H14	-3.93856	0.423222	-4.05963
O15	0.491375	0.069056	-1.93032
C16	1.412244	-0.50845	-2.51733
O17	1.388675	-1.2432	-3.56615
C18	2.840736	-0.33744	-1.94432
F19	3.599899	-1.41038	-2.19184
F20	3.422114	0.737893	-2.50091
F21	2.795071	-0.15191	-0.61341
H22	0.434857	-1.46069	-3.97056
C23	-1.85208	-1.88838	-4.10901
O24	-0.70749	-2.02719	-4.57503
C25	-2.96668	-2.81135	-4.66737
F26	-2.51143	-3.68647	-5.56392
F27	-3.54715	-3.50119	-3.65968

F28	-3.92803	-2.06282	-5.25445
C29	-4.046	1.638199	-0.99223
C30	-5.44573	1.822986	-0.8046
C31	-5.90975	2.267033	0.459897
C32	-5.01246	2.519758	1.472292
C33	-3.62278	2.370749	1.259372
C34	-3.12344	1.941418	0.042143
H35	-6.97744	2.395273	0.614243
H36	-5.36715	2.852361	2.443364
H37	-2.93226	2.607517	2.062278
C38	-1.85922	-0.82892	1.35784
C39	-2.17742	-1.79392	2.367211
C40	-1.76154	-1.58637	3.706699
C41	-1.04483	-0.46109	4.037765
C42	-0.73241	0.498274	3.049894
C43	-1.12444	0.349337	1.727137
H44	-2.01618	-2.3294	4.458363
H45	-0.72148	-0.29878	5.061916
H46	-0.17987	1.3892	3.334393
H47	-6.39674	0.824627	-3.92487
H48	-7.37579	1.665741	-1.78011
C49	-1.65526	1.896379	-0.24088
C50	-0.72743	1.358578	0.715021
C51	0.591122	1.777136	0.652652
C52	1.076124	2.71158	-0.29242
C53	0.203784	3.218639	-1.25237
C54	-1.15118	2.785701	-1.23536
H55	1.302109	1.339618	1.347897
H58	-1.86498	3.350038	-1.82784
C59	-0.99702	1.626297	-4.19529
H60	-1.20055	0.720586	-4.7446
H61	-1.74613	2.402932	-4.18306
H62	-0.01122	1.806324	-3.80061
O63	-0.31386	2.397416	-5.92724
C64	0.944277	2.6036	-5.8471
O65	1.720565	2.414274	-4.90473
C66	1.533697	3.155374	-7.17863
F67	0.768856	4.1415	-7.69173
F68	2.772321	3.647502	-7.01037
F69	1.604492	2.171403	-8.10214

C69	2.528496	3.121053	-0.25475
H70	2.637364	4.202107	-0.10578
H71	3.060383	2.613996	0.554339
H72	3.032606	2.8725	-1.19418
C72	0.654947	4.22408	-2.28032
H73	-0.19809	4.670044	-2.79926
H74	1.232137	5.033469	-1.81954
H75	1.291703	3.754467	-3.04128

Table S365. [Rh^{III}-
'(bisq^{Me2})(Me_{eq}...TFA)(TFA_{ax})(TFAH_{eq})][‡]
thermodynamic values

Temp	298.15	498.15
E_{gas}	-2840.26	-2840.26
E_{solv}	-2840.29	-2840.29
G	-2839.83	-2839.92
ZPE	328.703	328.703
H_{vib}	27.985	70.144
S_{trans}	45.983	48.533
S_{rot}	39.014	40.544
S_{vib}	186.075	292.516
solv	-18.8	-18.8

Table S366. [Rh^{III}-
'(bisq^{Me2})(Me_{eq}...TFA)(TFA_{eq})(TFAH_{ax})][‡] Cartesian
coordinates

Atom	x	y	z
Rh1	-1.27551	1.12532	-1.79884
N2	-2.01487	-0.90005	-0.04621
C3	-2.63769	-1.91633	-0.61372
C4	-3.02726	-3.08854	0.075325
C5	-2.73525	-3.18928	1.412987
C6	-6.03891	1.910333	-1.70017
C7	-5.4215	1.692741	-2.91005
C8	-4.02051	1.535684	-2.96001
N9	-3.26242	1.61228	-1.87149
H10	-2.84239	-1.81639	-1.67659
H11	-3.53493	-3.88553	-0.45867

H12	-3.00311	-4.07586	1.982974
O13	-1.91686	-0.38529	-3.3513
H14	-3.51602	1.303234	-3.88905
O15	0.776503	0.693953	-1.60635
C16	1.462677	-0.33262	-1.86532
O17	1.191202	-1.35483	-2.52322
C18	2.880635	-0.2811	-1.232
F19	3.626013	-1.33751	-1.56575
F20	3.533244	0.834236	-1.62793
F21	2.793555	-0.24348	0.117043
H22	0.251612	-1.478	-3.56418
C23	-1.52057	-1.12138	-4.26548
O24	-0.37793	-1.68206	-4.39039
C25	-2.5631	-1.56061	-5.31527
F26	-2.01908	-1.94478	-6.46332
F27	-3.23779	-2.6146	-4.78571
F28	-3.45733	-0.58899	-5.54859
C29	-3.84442	1.881394	-0.65413
C30	-5.25573	2.007428	-0.52185
C31	-5.80005	2.198642	0.774184
C32	-4.9665	2.270744	1.867535
C33	-3.56322	2.182216	1.715444
C34	-2.98852	1.994913	0.470752
H35	-6.87763	2.279462	0.887298
H36	-5.38375	2.410673	2.860502
H37	-2.92539	2.271602	2.588897
C38	-1.72903	-0.96837	1.289393
C39	-2.06779	-2.12273	2.067288
C40	-1.73245	-2.17953	3.443839
C41	-1.07313	-1.12822	4.034877
C42	-0.7385	0.014229	3.276356
C43	-1.05196	0.125567	1.929621
H44	-2.00378	-3.06343	4.015802
H45	-0.81273	-1.16601	5.088788
H46	-0.23105	0.841626	3.764431
H47	-5.98856	1.615628	-3.83133
H48	-7.11962	2.005041	-1.63291
C49	-1.50744	2.007591	0.258224
C50	-0.62369	1.31936	1.162714
C51	0.681924	1.759629	1.263658

C52	1.206353	2.847577	0.521039
C53	0.390635	3.495868	-0.39651
C54	-0.95937	3.059135	-0.54474
H55	1.360644	1.213944	1.912676
H58	-1.64803	3.731434	-1.04821
C59	-0.70346	2.410903	-3.66927
H60	-1.06648	1.532486	-4.17739
H61	-1.3423	3.274984	-3.55842
H62	0.338067	2.503001	-3.40227
O63	-0.22869	2.998925	-5.54919
C64	-0.49672	2.051589	-6.36099
O65	-1.02146	0.950846	-6.15245
C66	-0.07949	2.396367	-7.82052
F67	1.239338	2.672599	-7.89051
F68	-0.33197	1.387189	-8.66734
F69	-0.75003	3.482308	-8.26357
C69	2.655391	3.226381	0.704398
H70	2.788759	4.309631	0.79138
H71	3.074587	2.760482	1.600296
H72	3.252326	2.888766	-0.15095
C72	0.894726	4.644479	-1.23281
H73	0.097301	5.07933	-1.84041
H74	1.318545	5.442036	-0.61098
H75	1.690585	4.317984	-1.91385

Table S367. [Rh^{III}-
^l(bisq^{Me2})(Me_{eq}...TFA)(TFA_{eq})(TFAH_{ax})][‡]
thermodynamic values

Temp	298.15	498.15
E_{gas}	-2840.27	-2840.27
E_{solv}	-2840.29	-2840.29
G	-2839.83	-2839.92
ZPE	328.550	328.550
H_{vib}	27.443	69.216
S_{trans}	45.983	48.533
S_{rot}	38.944	40.474
S_{vib}	186.806	293.280
solv	-18.1	-18.1

Table S368. $[\text{Rh}^{\text{III-II}}(\text{bisq}^{\text{Me2}})(\text{Me}_{\text{ax}}\cdots\text{OVCl}_3)(\text{TFA})_2]^{\ddagger}$
Cartesian coordinates

Atom	x	y	z
Rh1	-1.663	0.130782	-2.15917
N2	-2.46888	-1.03826	-0.59226
C3	-3.35707	-1.99591	-0.83774
C4	-3.7669	-2.93665	0.125096
C5	-3.20791	-2.881	1.377802
C6	-6.33481	1.505649	-2.19987
C7	-5.7638	1.049629	-3.3631
C8	-4.37312	0.812504	-3.40065
N9	-3.57967	1.045096	-2.36033
H10	-3.75899	-2.05105	-1.84239
H11	-4.47897	-3.70275	-0.15907
H12	-3.4629	-3.61318	2.139153
H13	-3.88826	0.430344	-4.29295
O14	0.102582	-0.85336	-1.73298
C15	1.084703	-1.06991	-2.5495
O16	1.160802	-0.93513	-3.75834
C17	2.32072	-1.59585	-1.76251
F18	3.299641	-1.98963	-2.58112
F19	2.827501	-0.61823	-0.96043
F20	1.995509	-2.63341	-0.96587
O21	-0.74507	1.349385	-3.51945
C22	-1.10275	1.404212	-4.75294
O23	-2.00681	0.809871	-5.33155
C24	-0.27009	2.445505	-5.54555
F25	-0.26541	2.181447	-6.85548
F26	-0.8224	3.674974	-5.36976
F27	1.008576	2.522368	-5.12625
C28	-4.10365	1.629999	-1.22626
C29	-5.51084	1.818092	-1.08819
C30	-6.02379	2.321031	0.135652
C31	-5.16672	2.657163	1.158005
C32	-3.76785	2.556679	0.977788
C33	-3.22365	2.065836	-0.19477
H34	-7.09768	2.444768	0.243603
H35	-5.55708	3.04119	2.095618
H36	-3.10117	2.904553	1.761522

C37	-1.95536	-0.8974	0.680021
C38	-2.28516	-1.8534	1.692042
C39	-1.68654	-1.75727	2.973714
C40	-0.80611	-0.7399	3.248953
C41	-0.52548	0.232705	2.266567
C42	-1.08861	0.191517	1.0004
H43	-1.93604	-2.50214	3.724007
H44	-0.33671	-0.66548	4.225082
H45	0.138945	1.056372	2.510023
H46	-6.35617	0.823987	-4.24247
H47	-7.40957	1.645889	-2.1201
C48	-1.75539	2.174479	-0.47221
C49	-0.76895	1.301625	0.056829
C50	0.588685	1.604737	-0.18754
C51	0.989714	2.688576	-0.95503
C52	0.002417	3.569698	-1.46964
C53	-1.33414	3.302312	-1.20375
H54	1.337813	0.915276	0.182274
H57	-2.09368	3.972374	-1.59704
C58	-1.78944	-1.6988	-3.66468
H59	-0.9432	-1.40203	-4.26769
H60	-1.64852	-2.46846	-2.91955
H61	-2.77164	-1.30169	-3.87538
C61	0.386657	4.741096	-2.33496
H62	-0.47471	5.38091	-2.5417
H63	1.167146	5.353763	-1.8704
H64	0.776658	4.389752	-3.29664
C64	2.448074	2.891133	-1.28049
H65	2.597071	2.908013	-2.36644
H66	2.82588	3.84389	-0.88944
H67	3.058936	2.082867	-0.87379
O68	-2.29152	-3.12179	-5.08089
V69	-3.58498	-4.06631	-4.81807
Cl70	-3.16041	-5.24457	-2.99485
Cl71	-5.25791	-2.70873	-4.25124
Cl72	-4.16339	-5.33652	-6.48152

Table S369. $[\text{Rh}^{\text{III-II}}(\text{bisq}^{\text{Me2}})(\text{Me}_{\text{ax}}\cdots\text{OVCl}_3)(\text{TFA})_2]^{\ddagger}$
thermodynamic values

Temp	298.15	498.15
E _{gas}	-3840.84	-3840.84
E _{solv}	-3840.87	-3840.87
G	-3840.44	-3840.53
ZPE	309.454	309.454
H _{vib}	28.538	70.241
S _{trans}	46.187	48.737
S _{rot}	39.154	40.684
S _{vib}	190.721	296.113
solv	-18.6	-18.6

Table S370. [Rh^{III}-

II(bisq^{Me2})(Me_{ax}...OVCl₃)(TFA_{eq})(TFAH_{eq})]⁺⁺

Cartesian coordinates

Atom	x	y	z
Rh1	-1.69871	0.021921	-1.91215
N2	-2.32359	-0.92567	-0.1369
C3	-3.22637	-1.89873	-0.24574
C4	-3.60119	-2.73996	0.813344
C5	-2.98885	-2.57035	2.031167
C6	-6.25333	1.60099	-1.90388
C7	-5.75856	0.975119	-3.02543
C8	-4.39721	0.618536	-3.0626
N9	-3.55837	0.899289	-2.07041
H10	-3.67236	-2.03903	-1.22154
H11	-4.33957	-3.51473	0.641772
H12	-3.21843	-3.22056	2.870252
H13	-3.98866	0.080755	-3.90972
O14	0.104125	-1.07823	-1.57378
C15	1.325975	-0.98078	-1.78018
O16	1.960822	-0.15575	-2.51255
C17	2.230255	-1.95841	-0.99281
F18	3.401646	-2.14542	-1.59417
F19	2.446822	-1.42337	0.228726
F20	1.61903	-3.13748	-0.83724
O21	-1.35542	0.912247	-3.77302
C22	-0.36231	1.554068	-4.22484
O23	0.834425	1.511178	-3.87995
C24	-0.74451	2.554225	-5.34543

F25	0.328717	3.143857	-5.87237
F26	-1.42812	1.935584	-6.31799
F27	-1.53754	3.511904	-4.81283
H28	1.366332	0.560734	-3.06588
C29	-3.98804	1.65965	-1.00384
C30	-5.37369	1.965417	-0.85412
C31	-5.8039	2.642653	0.316287
C32	-4.88781	3.03157	1.2653
C33	-3.50565	2.821976	1.050711
C34	-3.03748	2.160235	-0.07087
H35	-6.86073	2.859569	0.43937
H36	-5.21472	3.549974	2.16103
H37	-2.79006	3.229616	1.758711
C38	-1.75384	-0.66787	1.095579
C39	-2.05027	-1.52699	2.205019
C40	-1.41	-1.3215	3.453498
C41	-0.5205	-0.28829	3.611081
C42	-0.27035	0.588375	2.536348
C43	-0.86824	0.436772	1.292557
H44	-1.64003	-1.99368	4.274495
H45	-0.024	-0.12554	4.562135
H46	0.395418	1.432053	2.689212
H47	-6.39433	0.716966	-3.86448
H48	-7.30968	1.839361	-1.81871
C49	-1.57521	2.195636	-0.41698
C50	-0.56629	1.456381	0.252083
C51	0.77979	1.800874	0.016564
C52	1.160695	2.838223	-0.8307
C53	0.153737	3.582627	-1.50001
C54	-1.17593	3.243433	-1.28179
H55	1.5527	1.21734	0.50921
H58	-1.95193	3.823543	-1.77327
C59	-2.05695	-1.98269	-3.34059
H60	-1.52027	-1.45287	-4.11423
H61	-1.51335	-2.55576	-2.60536
H62	-3.12501	-1.85041	-3.25509
O63	-2.31553	-3.56561	-4.41515
V64	-3.08644	-3.58767	-5.85848
Cl65	-3.4811	-5.59954	-6.47232
Cl66	-4.93559	-2.48485	-5.52566

Cl67	-1.82419	-2.52276	-7.24536
C67	2.618629	3.14466	-1.05441
H68	2.851109	4.186204	-0.8046
H69	3.261854	2.499651	-0.45175
H70	2.888366	3.004117	-2.1078
C70	0.512156	4.708623	-2.43726
H71	1.122615	5.46861	-1.93696
H72	1.094857	4.338403	-3.28852
H73	-0.38116	5.196819	-2.83217

Table S371. [Rh^{III}-
^{II}(bisq^{Me2})(Me_{ax}...OVCl₃)(TFA_{eq})(TFAH_{eq})]⁺⁺
thermodynamic values

Temp	298.15	498.15
E_{gas}	-3841.24	-3841.24
E_{solv}	-3841.29	-3841.29
G	-3840.85	-3840.94
ZPE	316.407	316.407
H_{vib}	27.937	69.365
S_{trans}	46.190	48.740
S_{rot}	39.289	40.819
S_{vib}	190.031	295.706
solv	-36.6	-36.6

Table S372. [Rh^{III-II}(bisq^{Me2})(Me_{eq}...OVCl₃)(TFA)₂]⁺
Cartesian coordinates

Atom	x	y	z
Rh1	-1.25143	0.221514	-2.13975
N2	-2.03488	-0.99456	-0.41328
C3	-2.75884	-2.0584	-0.72808
C4	-3.28125	-2.94399	0.236564
C5	-3.02069	-2.7061	1.562626
C6	-5.83353	1.873	-2.24918
C7	-5.3718	1.086949	-3.27781
C8	-4.02358	0.673227	-3.27866
N9	-3.16569	1.05128	-2.33939
H10	-2.90738	-2.23385	-1.788
H11	-3.86449	-3.79849	-0.08877

H12	-3.39581	-3.36935	2.337535
O13	-1.89533	-1.25684	-3.39338
H14	-3.64012	-0.00918	-4.02823
O15	0.507924	-0.78195	-1.81094
C16	1.646092	-0.4267	-2.29474
O17	1.947564	0.542582	-2.98256
C18	2.790382	-1.35322	-1.80455
F19	3.799357	-1.39322	-2.68142
F20	3.279715	-0.84656	-0.63686
F21	2.392112	-2.61084	-1.5605
C22	-1.15267	-1.91915	-4.24172
O23	-0.00723	-1.74041	-4.59071
C24	-2.0061	-3.06401	-4.85659
F25	-1.29416	-3.82394	-5.68758
F26	-2.5119	-3.86217	-3.88431
F27	-3.05445	-2.55098	-5.54059
C28	-3.5778	1.890111	-1.33038
C29	-4.94222	2.291849	-1.22916
C30	-5.34319	3.08392	-0.12393
C31	-4.42123	3.465056	0.823497
C32	-3.06135	3.106214	0.682906
C33	-2.62217	2.33771	-0.38061
H34	-6.3841	3.383792	-0.04218
H35	-4.72773	4.06901	1.672103
H36	-2.33786	3.463164	1.410024
C37	-1.74771	-0.72433	0.901823
C38	-2.23419	-1.58836	1.935284
C39	-1.9045	-1.3294	3.289302
C40	-1.10363	-0.2621	3.613605
C41	-0.61602	0.584221	2.596371
C42	-0.92598	0.388801	1.259244
H43	-2.28559	-1.99699	4.056526
H44	-0.83984	-0.06376	4.647888
H45	0.016827	1.425215	2.863913
H46	-6.02231	0.758672	-4.08059
H47	-6.87432	2.182077	-2.20501
C48	-1.14954	2.120887	-0.60372
C49	-0.34594	1.327621	0.262624
C50	1.04474	1.512307	0.252845
C51	1.67442	2.441771	-0.57265

C52	0.888445	3.242892	-1.4407
C53	-0.48937	3.078059	-1.426
H54	1.654414	0.871545	0.881026
H57	-1.10126	3.722014	-2.05232
C58	-0.74933	1.388651	-4.15407
H59	-1.15459	0.689528	-4.87
H60	-1.34879	2.242909	-3.88548
H61	0.285907	1.279127	-3.82933
C61	3.174987	2.542306	-0.5878
H62	3.552335	2.182818	-1.55216
H63	3.513546	3.57692	-0.46551
H64	3.624917	1.931741	0.197587
C64	1.527584	4.227132	-2.38633
H65	0.774326	4.788845	-2.94301
H66	2.170418	4.940564	-1.85782
H67	2.156673	3.698679	-3.11236
O68	0.051721	2.549317	-5.72239
V69	-0.971	3.610608	-6.40268
Cl70	-0.11921	4.824994	-7.99998
Cl71	-2.73149	2.46758	-7.10819
Cl72	-1.7291	4.920549	-4.75968

Table S373. $[\text{Rh}^{\text{III-II}}(\text{bisq}^{\text{Me2}})(\text{Me}_{\text{eq}}\cdots\text{OVCl}_3)(\text{TFA})_2]^{\dagger}$
thermodynamic values

Temp	298.15	498.15
E _{gas}	-3840.83	-3840.83
E _{solv}	-3840.86	-3840.86
G	-3840.43	-3840.53
ZPE	309.181	309.181
H _{vib}	28.088	69.398
S _{trans}	46.187	48.737
S _{rot}	39.193	40.723
S _{vib}	192.226	297.631
solv	-18.7	-18.7

Table S374. $[\text{Rh}^{\text{III-}}(\text{bisq}^{\text{Me2}})(\text{Me}_{\text{eq}}\cdots\text{OVCl}_3)(\text{TFA}_{\text{ax}})(\text{TFAH}_{\text{eq}})]^{+\dagger}$
Cartesian coordinates

Atom	x	y	z
Rh1	-1.57637	0.602283	-1.81304
N2	-2.20146	-0.8753	-0.07186
C3	-2.87515	-1.94099	-0.48748
C4	-3.31445	-2.96819	0.370456
C5	-3.02236	-2.87653	1.708636
C6	-6.26927	1.754348	-1.72529
C7	-5.7487	1.150935	-2.84713
C8	-4.37143	0.861136	-2.90219
N9	-3.53924	1.186392	-1.91651
H10	-3.06478	-2.00257	-1.55307
H11	-3.85892	-3.81088	-0.04131
H12	-3.32709	-3.65283	2.40517
O13	-2.13726	-0.90212	-3.17048
H14	-3.94776	0.32101	-3.73882
O15	0.484999	0.108429	-1.53155
C16	1.472355	-0.42516	-2.05605
O17	1.579833	-1.0125	-3.18604
C18	2.806074	-0.341	-1.27289
F19	3.663564	-1.28313	-1.64999
F20	3.354237	0.869152	-1.50376
F21	2.577001	-0.45674	0.043393
H22	0.686864	-1.10822	-3.73746
C23	-1.59036	-1.49685	-4.15144
O24	-0.41937	-1.44241	-4.55708
C25	-2.60312	-2.37858	-4.92832
F26	-2.03239	-3.04364	-5.92385
F27	-3.17827	-3.25718	-4.08356
F28	-3.57734	-1.58796	-5.43205
C29	-4.01755	1.840706	-0.80275
C30	-5.4095	2.109533	-0.6565
C31	-5.86397	2.707266	0.546737
C32	-4.96778	3.025252	1.541881
C33	-3.5843	2.797102	1.361211
C34	-3.09567	2.221795	0.20135
H35	-6.92468	2.906015	0.667856
H36	-5.31547	3.477903	2.465102
H37	-2.88878	3.101262	2.137701
C38	-1.91381	-0.73781	1.265486
C39	-2.30537	-1.75629	2.195405

C40	-1.96593	-1.64028	3.567443
C41	-1.25289	-0.55507	4.014711
C42	-0.87061	0.452856	3.106469
C43	-1.18999	0.397115	1.75691
H44	-2.27553	-2.42622	4.250375
H45	-0.98642	-0.46239	5.06272
H46	-0.32479	1.315392	3.477323
H47	-6.37649	0.869625	-3.68508
H48	-7.33286	1.960938	-1.64559
C49	-1.61656	2.139995	-0.0554
C50	-0.73372	1.492392	0.871271
C51	0.589669	1.914031	0.935843
C52	1.104172	2.954048	0.142124
C53	0.268922	3.574675	-0.81017
C54	-1.06432	3.159111	-0.88964
H55	1.264709	1.399068	1.611901
H58	-1.7438	3.708932	-1.53558
C59	-0.96748	1.879787	-3.89295
H60	-0.14419	2.371747	-3.39729
H61	-0.79377	0.935703	-4.38259
H62	-1.95904	2.303042	-3.83186
O63	-0.67884	2.774786	-5.59963
V64	-0.75484	4.381327	-5.90187
Cl65	-1.39888	4.73109	-7.91573
Cl66	-2.23965	5.146646	-4.49454
Cl67	1.194037	5.209526	-5.45047
C67	2.535131	3.388871	0.312756
H68	2.589455	4.44096	0.617489
H69	3.049888	2.788973	1.065914
H70	3.091016	3.302391	-0.62676
C70	0.774773	4.699743	-1.67903
H71	-0.01581	5.101014	-2.31647
H72	1.164262	5.524786	-1.07155
H73	1.597018	4.375105	-2.32809

Table S375. [Rh^{III}-

^{II}(bisq^{Me2})(Me_{eq}...OVCl₃)(TFA_{ax})(TFAH_{eq})]⁺⁺

thermodynamic values

Temp	298.15	498.15
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E_{gas}	-3841.22	-3841.22
E_{solv}	-3841.28	-3841.28
G	-3840.84	-3840.93
ZPE	316.720	316.720
H_{vib}	28.072	69.519
S_{trans}	46.190	48.740
S_{rot}	39.313	40.843
S_{vib}	191.791	297.523
solv	-36.3	-36.3

Table S376. [Rh^{III}-

^{II}(bisq^{Me2})(Me_{eq}...OVCl₃)(TFA_{eq})(TFAH_{ax})]⁺⁺

Cartesian coordinates

Atom	x	y	z
Rh1	-1.455	0.727471	-1.65688
N2	-2.19918	-0.72307	-0.05961
C3	-2.96077	-1.71932	-0.49428
C4	-3.37364	-2.79029	0.320496
C5	-2.95446	-2.8172	1.628318
C6	-6.08228	2.13917	-1.63607
C7	-5.54614	1.656889	-2.80827
C8	-4.17839	1.322664	-2.85714
N9	-3.3686	1.49637	-1.81676
H10	-3.24269	-1.68708	-1.54134
H11	-3.99385	-3.57461	-0.09917
H12	-3.22992	-3.63497	2.288462
O13	-2.07339	-0.62714	-3.21257
H14	-3.749	0.869493	-3.74092
O15	0.462932	-0.00113	-1.28085
C16	1.38169	-0.47715	-2.00413
O17	1.364984	-0.83761	-3.1986
C18	2.746353	-0.55629	-1.27024
F19	3.612502	-1.33809	-1.90641
F20	3.262942	0.692381	-1.19467
F21	2.585172	-1.01217	-0.01625
H22	0.298501	-1.14757	-3.91894
C23	-1.67927	-1.30164	-4.186
O24	-0.49673	-1.52771	-4.57986
C25	-2.8103	-1.93603	-5.03077

F26	-2.34874	-2.70195	-6.00813
F27	-3.59568	-2.67043	-4.22079
F28	-3.55835	-0.94584	-5.55701
C29	-3.85711	2.055762	-0.65711
C30	-5.24322	2.348082	-0.51321
C31	-5.70929	2.827845	0.737933
C32	-4.82624	3.022017	1.775607
C33	-3.44229	2.791091	1.595337
C34	-2.94484	2.322297	0.393107
H35	-6.76738	3.039467	0.860194
H36	-5.18284	3.386165	2.733922
H37	-2.75636	3.014068	2.406649
C38	-1.78846	-0.69666	1.250934
C39	-2.14535	-1.76944	2.131685
C40	-1.68348	-1.776	3.47256
C41	-0.88944	-0.75547	3.934808
C42	-0.54436	0.306962	3.075603
C43	-0.97677	0.370898	1.757826
H44	-1.96638	-2.60157	4.119122
H45	-0.52999	-0.75446	4.958748
H46	0.064135	1.118238	3.463396
H47	-6.15618	1.49936	-3.69052
H48	-7.14181	2.365141	-1.55983
C49	-1.46496	2.268352	0.118674
C50	-0.55258	1.531084	0.940103
C51	0.786076	1.930209	0.972515
C52	1.271655	3.040812	0.271309
C53	0.38611	3.790612	-0.5459
C54	-0.94318	3.393193	-0.59876
H55	1.49057	1.329645	1.538683
H58	-1.64802	3.995882	-1.16607
C59	-0.41054	2.057625	-3.43718
H60	-0.40931	1.213622	-4.1089
H61	-1.2746	2.701773	-3.37495
H62	0.44473	2.237496	-2.80679
C62	0.859003	4.9973	-1.32031
H63	0.033779	5.474656	-1.85413
H64	1.308639	5.745892	-0.65811
H65	1.622694	4.729139	-2.06009
C65	2.723493	3.421227	0.372136

H66	2.834723	4.440324	0.761568
H67	3.274431	2.741376	1.024172
H68	3.202667	3.406667	-0.61339
O69	0.381246	3.20992	-4.8229
V70	-0.56679	3.709003	-6.06184
Cl71	-1.34519	1.892243	-6.97498
Cl72	-2.20656	4.813997	-5.13069
Cl73	0.505362	4.922359	-7.46762

Table S377. $[\text{Rh}^{\text{III}}\text{-(bisq}^{\text{Me2}})(\text{Me}_{\text{eq}}\cdots\text{OVCl}_3)(\text{TFA}_{\text{eq}})(\text{TFAH}_{\text{ax}})]^{++}$
thermodynamic values

Temp	298.15	498.15
E_{gas}	-3841.22	-3841.22
E_{solv}	-3841.28	-3841.28
G	-3840.84	-3840.93
ZPE	315.675	315.675
H_{vib}	27.667	68.759
S_{trans}	46.190	48.740
S_{rot}	39.206	40.736
S_{vib}	193.323	299.154
solv	-36.7	-36.7

Table S378.
 $[\text{Rh}^{\text{III}}(\text{bisq}^{\text{Me2}})(\text{CH}_2\text{TFA}_{\text{ax}}\cdots\text{H}\cdots\text{TFA}_{\text{eq}})(\text{TFA}_{\text{eq}})]^{++}$
Cartesian coordinates

Atom	x	y	z
Rh1	-2.76912	0.363172	-1.48048
N2	-1.62165	-0.72991	-0.02605
C3	-1.94177	-2.01334	0.124509
C4	-1.24196	-2.90433	0.954406
C5	-0.16062	-2.43566	1.657063
C11	-6.29271	-0.21334	1.845206
C12	-6.45263	-0.82261	0.622962
C13	-5.4805	-0.62553	-0.37779
N14	-4.42115	0.15603	-0.20483
H15	-2.78773	-2.36955	-0.44461
H16	-1.56298	-3.9379	1.001063

H17	0.426187	-3.09194	2.293359
H23	-5.56555	-1.1468	-1.32068
O28	-1.05336	0.777976	-2.57661
C29	-0.50716	-0.18832	-3.17573
O30	-0.93515	-1.36679	-3.21627
C31	0.815753	0.159541	-3.89569
F32	1.387519	-0.9213	-4.41754
F33	0.579721	1.05034	-4.86498
F34	1.663329	0.712295	-3.00354
O35	-3.96869	1.430534	-2.76429
C36	-3.79227	1.357583	-4.05371
O37	-2.98812	0.693078	-4.68261
C38	-4.85416	2.211337	-4.80012
F39	-4.58506	2.289917	-6.10176
F40	-6.06987	1.648307	-4.6442
F41	-4.91286	3.465948	-4.30228
H42	-2.18629	-1.28157	-2.83658
C43	-3.53206	-1.48849	-2.90637
H44	-3.29046	-1.79437	-3.93044
H46	-4.39382	-0.83491	-2.96977
C41	0.197369	-1.07038	1.557865
C42	-0.57606	-0.20844	0.713216
C35	-0.22931	1.175936	0.646952
C44	0.871903	1.626014	1.365134
C45	1.64558	0.771513	2.173247
C46	1.307484	-0.55547	2.274959
H50	1.123563	2.681075	1.322733
H51	2.494162	1.170794	2.71901
H52	1.881634	-1.23246	2.900368
C47	-4.27969	0.849792	0.97861
C48	-5.18716	0.646704	2.059224
C49	-4.94819	1.313559	3.287936
C50	-3.86898	2.156751	3.419785
C51	-3.01705	2.403361	2.319199
C52	-3.21249	1.774482	1.102224
H55	-5.63116	1.149992	4.115747
H56	-3.68475	2.665715	4.360496
H57	-2.21184	3.125107	2.42108
H53	-7.00566	-0.37667	2.648379
H54	-7.2938	-1.47431	0.415827

C55	-0.99596	2.156808	-0.14581
C56	-2.43633	2.201409	-0.11917
C57	-3.06883	3.23916	-0.88942
C58	-2.37374	4.147431	-1.66518
C59	-0.95394	4.060709	-1.68857
C60	-0.30699	3.070316	-0.93896
H58	-4.1501	3.311711	-0.83585
H61	0.771504	2.982009	-1.01947
O62	-3.9153	-2.64088	-2.13326
C63	-3.68878	-3.86698	-2.65755
O64	-3.20187	-4.11665	-3.72322
C65	-4.16857	-4.93084	-1.64498
F66	-3.49158	-4.7866	-0.47631
F67	-5.47477	-4.77088	-1.38145
F68	-3.95657	-6.15225	-2.11049
C68	-3.10222	5.203904	-2.45618
H69	-2.93337	5.08075	-3.53117
H70	-4.17877	5.148945	-2.28784
H71	-2.76298	6.210308	-2.1867
C71	-0.14857	5.006643	-2.53131
H72	-0.35683	6.048987	-2.26199
H73	0.923707	4.82986	-2.42972
H74	-0.41511	4.9013	-3.59027

Table S379.

$[\text{Rh}^{\text{III}}(\text{bisq}^{\text{Me2}})(\text{CH}_2\text{TFA}_{\text{ax}}\cdots\text{H}\cdots\text{TFA}_{\text{eq}})(\text{TFA}_{\text{eq}})]^{+\ddagger}$
thermodynamic values

Temp	298.15	498.15
E _{gas}	-2839.42	-2839.42
E _{solv}	-2839.49	-2839.49
G	-2839.04	-2839.12
ZPE	322.292	322.292
H _{vib}	26.896	68.473
S _{trans}	45.979	48.529
S _{rot}	38.704	40.234
S _{vib}	176.661	281.605
solv	-44.6	-44.6

Table S380.

$$[\text{Rh}^{\text{III}}(\text{bisq}^{\text{Me}_2})(\text{CH}_2\text{TFA}_{\text{eq}}\cdots\text{H}\cdots\text{TFA}_{\text{ax}})(\text{TFA}_{\text{eq}})]^{++}$$

Cartesian coordinates

Atom	x	y	z
Rh1	-1.43537	0.224056	-1.62565
N2	-2.08962	-1.13784	-0.17177
C3	-2.49024	-2.36684	-0.47182
C4	-2.96485	-3.25974	0.509309
C5	-3.02559	-2.84987	1.820899
C11	-6.15697	1.676436	-1.53704
C12	-5.68449	0.694784	-2.37116
C13	-4.30899	0.411928	-2.37155
N14	-3.42041	1.051816	-1.61111
H15	-2.43959	-2.6523	-1.51499
H16	-3.279	-4.25261	0.208006
H17	-3.40065	-3.51231	2.59543
H22	-3.91887	-0.37168	-3.00651
O27	0.306983	-0.85068	-1.51412
C28	1.463916	-0.44393	-1.94222
O29	1.753051	0.582737	-2.53267
C30	2.578156	-1.43935	-1.51664
F31	2.818762	-1.26516	-0.18819
F32	2.216617	-2.71652	-1.70411
F33	3.712356	-1.21026	-2.17575
H34	0.173275	1.905042	-3.78772
H35	-0.50169	0.487832	-3.61075
O36	-2.01158	-1.1871	-3.04862
C37	-1.29253	-1.29327	-4.09141
O38	-0.38913	-0.50424	-4.43084
C39	-1.64031	-2.49699	-4.99538
F40	-0.7611	-2.6372	-5.9784
F41	-1.66446	-3.61615	-4.25429
F42	-2.86371	-2.29864	-5.51412
C43	-0.78192	1.767406	-3.26534
H45	-0.77093	2.498546	-2.46518
C41	-5.25112	2.397373	-0.72447
C42	-3.85673	2.070001	-0.7802
C35	-2.94303	2.850309	-0.0129
C44	-3.43036	3.892105	0.762505

C45	-4.80458	4.191956	0.840075
C46	-5.70068	3.455103	0.10636
H50	-2.72463	4.488909	1.33247
H51	-5.14225	5.00916	1.468989
H52	-6.76264	3.679979	0.132148
C47	-2.08522	-0.71193	1.131676
C48	-2.58045	-1.5521	2.173255
C49	-2.58701	-1.06066	3.502714
C50	-2.10395	0.19874	3.775305
C51	-1.57874	1.002328	2.738461
C52	-1.56022	0.56657	1.424178
H55	-2.96812	-1.69538	4.297134
H56	-2.10275	0.575762	4.793024
H57	-1.16161	1.975713	2.981142
H53	-7.21396	1.923808	-1.50003
H54	-6.33828	0.132856	-3.02804
C55	-1.47629	2.640161	-0.05277
C56	-0.8756	1.410189	0.374488
C57	0.557667	1.354959	0.388134
C58	1.365981	2.409171	-0.00201
C59	0.741476	3.623083	-0.40357
C60	-0.65641	3.705322	-0.43307
H58	1.019414	0.44195	0.74991
H61	-1.12503	4.617526	-0.78734
O62	-1.84676	2.045145	-4.20282
C63	-2.57751	3.145344	-4.01966
O64	-2.46296	3.960388	-3.13734
C65	-3.66119	3.226003	-5.11852
F66	-3.10893	3.207785	-6.33647
F67	-4.48902	2.161615	-5.00968
F68	-4.37988	4.337409	-4.97651
C68	1.570719	4.808358	-0.8101
H69	2.241326	5.113972	0.001908
H70	2.212815	4.559553	-1.66361
H71	0.94916	5.662853	-1.08437
C71	2.867558	2.278049	0.017551
H72	3.279375	2.418972	-0.98739
H73	3.328626	3.025876	0.67258
H74	3.171629	1.287166	0.358711

Table S381.

$[\text{Rh}^{\text{III}}(\text{bisq}^{\text{Me2}})(\text{CH}_2\text{TFA}_{\text{eq}}\cdots\text{H}\cdots\text{TFA}_{\text{ax}})(\text{TFA}_{\text{eq}})]^{++}$
thermodynamic values

Temp	298.15	498.15
E _{gas}	-2839.43	-2839.43
E _{solv}	-2839.50	-2839.50
G	-2839.04	-2839.12
ZPE	322.696	322.696
H _{vib}	26.724	68.215
S _{trans}	45.979	48.529
S _{rot}	38.620	40.150
S _{vib}	174.970	279.691
solv	-42.0	-42.0

Table S382.

$[\text{Rh}^{\text{III}}(\text{bisq}^{\text{Me2}})(\text{CH}_2\text{TFA}_{\text{eq}}\cdots\text{H}\cdots\text{TFA}_{\text{eq}})(\text{TFA}_{\text{ax}})]^{++}$
Cartesian coordinates

Atom	x	y	z
Rh1	-2.71393	0.14881	-1.30917
N2	-1.66624	-1.01159	0.116462
C3	-2.07208	-2.25823	0.339045
C4	-1.41155	-3.12909	1.223554
C5	-0.28935	-2.68591	1.879271
C11	-5.97221	0.258405	2.289294
C12	-6.25171	-0.45245	1.144585
C13	-5.34734	-0.40617	0.06508
N14	-4.24681	0.338983	0.101414
H15	-2.93058	-2.59046	-0.23052
H16	-1.79363	-4.13511	1.354191
H17	0.257053	-3.33443	2.558183
H23	-5.49141	-1.0073	-0.82526
O28	-1.09453	-0.2825	-2.53391
C29	-1.08215	0.281331	-3.66642
O30	-1.92661	1.102745	-4.08632
C31	0.151885	-0.01323	-4.54666
F32	1.131615	0.848319	-4.17551
F33	0.593884	-1.25737	-4.3612
F34	-0.1145	0.177931	-5.83462

H35	-4.04612	2.247422	-3.40673
H36	-2.92288	1.111546	-3.19724
O37	-3.64194	-1.54696	-1.88124
C38	-3.62393	-2.06218	-3.08904
O39	-3.1095	-1.6487	-4.10153
C40	-4.41376	-3.40311	-3.0521
F41	-4.48116	-3.96083	-4.25341
F42	-3.80038	-4.26372	-2.20612
F43	-5.66528	-3.20107	-2.58988
C44	-4.16976	1.383381	-2.73962
H46	-4.59441	1.764951	-1.81832
C41	-3.97131	1.121346	1.199515
C42	-4.81071	1.069106	2.351251
C43	-4.45266	1.831028	3.492506
C36	-3.32461	2.619006	3.472168
C45	-2.53504	2.708118	2.302685
C46	-2.84324	1.979917	1.166937
H49	-5.08456	1.78603	4.374607
H50	-3.0495	3.201547	4.345569
H51	-1.683	3.381477	2.286594
C48	-0.55136	-0.52229	0.763274
C49	0.176387	-1.36735	1.660251
C50	1.351003	-0.87987	2.287293
C51	1.797973	0.393142	2.029799
C52	1.077128	1.22382	1.147451
C53	-0.08723	0.801178	0.523869
H55	1.892827	-1.536	2.961367
H56	2.701373	0.767301	2.50035
H57	1.434033	2.231869	0.95857
H53	-7.13835	-1.07064	1.060061
H54	-6.63371	0.210858	3.149854
C55	-0.78464	1.759421	-0.37582
C56	-2.10461	2.229272	-0.1222
C57	-2.57899	3.321876	-0.9103
C58	-1.83959	3.909107	-1.92114
C59	-0.53046	3.405075	-2.18752
C60	-0.04045	2.360614	-1.41371
H58	-3.55714	3.729762	-0.66835
H61	0.952099	1.973662	-1.62038
O62	-5.12838	0.485913	-3.30818

C63	-5.44832	0.68342	-4.60482
O64	-5.02057	1.54756	-5.3203
C65	-6.50707	-0.35461	-5.03773
F66	-7.59501	-0.24253	-4.25289
F67	-6.8597	-0.14765	-6.30155
F68	-6.02881	-1.60494	-4.9152
C68	-2.40301	5.060336	-2.71606
H69	-1.76812	5.949954	-2.63552
H70	-2.46733	4.813197	-3.78224
H71	-3.40395	5.330277	-2.37087
C71	0.302044	3.987873	-3.29639
H72	-0.19046	3.837371	-4.26446
H73	0.432893	5.06849	-3.17015
H74	1.287914	3.523131	-3.34559

Table S383.

$[\text{Rh}^{\text{III}}(\text{bisq}^{\text{Me2}})(\text{CH}_2\text{TFA}_{\text{eq}}\cdots\text{H}\cdots\text{TFA}_{\text{eq}})(\text{TFA}_{\text{ax}})]^{+\ddagger}$
thermodynamic values

Temp	298.15	498.15
E_{gas}	-2839.43	-2839.43
E_{solv}	-2839.50	-2839.50
G	-2839.04	-2839.13
ZPE	322.540	322.540
H_{vib}	26.117	67.220
S_{trans}	45.979	48.529
S_{rot}	38.618	40.148
S_{vib}	175.203	279.947
solv	-44.1	-44.1

Rh(bisq^{Me4}) complexes

Table S384. Rh^I(bisq^{Me4})(TFA)(TFAH) Cartesian coordinates

Atom	x	y	z
Rh1	-1.12445	0.545094	-1.58709
N2	-1.74687	-0.7285	-0.05029
C3	-2.08617	-1.93476	-0.50626
C4	-2.86433	-2.85234	0.224307

C5	-3.31555	-2.49173	1.470727
C6	-5.53753	2.601933	-1.59617
C7	-5.09301	1.693236	-2.52352
C8	-3.76897	1.227258	-2.43028
N9	-2.90864	1.617691	-1.48976
H10	-1.74241	-2.17128	-1.50616
H11	-3.1114	-3.81104	-0.21924
H12	-3.95087	-3.1526	2.054568
H13	-3.38704	0.502504	-3.13916
O14	0.525921	-0.77634	-1.75062
C15	1.746864	-0.59807	-1.83649
O16	2.402614	0.457045	-2.14073
C17	2.664623	-1.79392	-1.50057
F18	3.649797	-1.92517	-2.39983
F19	3.233696	-1.59574	-0.28583
F20	1.979713	-2.94264	-1.45012
O21	-0.80458	1.689639	-3.33571
C22	0.188448	2.37489	-3.66116
O23	1.365829	2.360366	-3.21127
C24	-0.03547	3.396916	-4.80171
F25	0.423078	4.613742	-4.43743
F26	0.634617	3.019282	-5.90822
F27	-1.33041	3.527516	-5.12652
H28	1.818957	1.313054	-2.53611
C29	-3.29894	2.583858	-0.58189
C30	-4.6473	3.080046	-0.60479
C31	-5.06675	4.053357	0.336563
C32	-4.17834	4.550435	1.256885
C33	-2.8431	4.0974	1.250376
C34	-2.37726	3.138088	0.364243
H35	-6.09549	4.401938	0.301809
H36	-4.4891	5.300776	1.97806
H37	-2.1369	4.523284	1.95744
C39	-2.07996	-0.38536	1.244694
C40	-2.92344	-1.2473	2.021719
C41	-3.32049	-0.85947	3.326532
C42	-2.86378	0.318158	3.865308
C43	-1.96988	1.125275	3.130024
C44	-1.55878	0.803162	1.847019
H45	-3.975	-1.51875	3.890569

H46	-3.16111	0.619189	4.865713
H47	-1.56327	2.021026	3.590208
H49	-5.73318	1.320062	-3.31567
H50	-6.55693	2.978182	-1.61601
C51	-0.91905	2.790164	0.444489
C52	-0.51932	1.665394	1.194744
C53	0.843784	1.397474	1.395393
C54	1.816126	2.255151	0.827927
C55	1.417535	3.392385	0.103006
C56	0.04271	3.658802	-0.09713
C58	2.424482	4.343545	-0.51295
H59	2.091868	5.382085	-0.43192
H60	3.404933	4.285934	-0.04011
H61	2.551896	4.128898	-1.58174
C61	3.276742	1.889967	1.011828
H62	3.941904	2.486191	0.389261
H63	3.598324	2.014307	2.054691
H64	3.452285	0.843346	0.746716
C64	-0.36852	4.857151	-0.92851
H65	0.153421	4.868481	-1.89021
H66	-1.43936	4.86362	-1.13309
H67	-0.12674	5.803194	-0.42638
C67	1.297304	0.187464	2.187087
H68	1.797203	-0.5452	1.54255
H69	2.019579	0.464966	2.963639
H70	0.465014	-0.31882	2.676763

Table S385. Rh^I(bisq^{Me4})(TFA)(TFAH) thermodynamic values

Temp	298.15	498.15
E _{gas}	-2352.86	-2352.86
E _{solv}	-2352.87	-2352.87
G	-2352.41	-2352.49
ZPE	321.667	321.667
H _{vib}	24.050	61.761
S _{trans}	45.594	48.145
S _{rot}	38.000	39.530
S _{vib}	157.549	252.676
solv	-11.5	-11.5

Table S386. Rh^I(bisq^{Me4})(κ¹-TFA) Cartesian coordinates

Atom	x	y	z
Rh1	-0.77231	0.898522	-1.93774
N2	-1.74006	-1.07582	0.189249
C3	-2.44504	-2.12318	-0.18664
C4	-3.40214	-2.76485	0.638234
C5	-3.59899	-2.28363	1.909739
C6	-5.19652	2.742071	-2.00995
C7	-4.74423	1.985417	-3.06836
C8	-3.42428	1.491979	-3.06317
N9	-2.58342	1.729941	-2.05828
H10	-2.2486	-2.49467	-1.19178
H11	-3.95297	-3.62265	0.264407
H12	-4.31487	-2.75005	2.582715
H13	-3.03351	0.883653	-3.87215
O14	0.913772	-0.51933	-2.20532
C15	0.177766	-1.16783	-2.99381
O16	-0.96604	-0.7663	-3.36329
C17	0.626333	-2.55457	-3.48358
F18	1.933361	-2.76472	-3.27613
F19	-0.06151	-3.51012	-2.81497
F20	0.375532	-2.71274	-4.79526
C21	-4.32541	3.013437	-0.92365
C22	-3.00769	2.480797	-0.98302
C23	-2.06589	2.6941	0.053601
C24	-2.46125	3.455452	1.138568
C25	-3.76903	3.988469	1.221402
C26	-4.68714	3.774456	0.217183
H27	-1.75812	3.64698	1.941881
H28	-4.04726	4.57432	2.092849
H29	-5.69253	4.181191	0.284666
C30	-2.85118	-1.16517	2.361867
C31	-1.92618	-0.57161	1.442947
C32	-1.14815	0.560476	1.858813
C33	-1.29353	1.016415	3.157085
C34	-2.20322	0.424914	4.063893
C35	-2.97796	-0.6412	3.673133

H36	-0.68642	1.854281	3.489248
H37	-2.28553	0.820863	5.072328
H38	-3.68416	-1.1011	4.360438
H39	-5.38493	1.759476	-3.91426
H40	-6.20966	3.133576	-1.99387
C41	-0.69117	2.103021	-0.1077
C42	-0.18123	1.212	0.917247
C43	1.170568	0.924861	0.979022
C44	2.084837	1.552427	0.062849
C45	1.630718	2.399725	-0.93313
C46	0.222168	2.712153	-1.05111
C47	2.603845	3.013243	-1.92023
H48	2.096479	3.397621	-2.80513
H49	3.168135	3.847083	-1.47926
H50	3.332126	2.274227	-2.26532
C51	3.559035	1.229292	0.187711
H52	4.190592	2.000295	-0.25533
H53	3.862188	1.121954	1.23255
H54	3.795849	0.28109	-0.31371
C55	-0.15777	3.976288	-1.81197
H56	0.08164	3.899263	-2.87518
H57	-1.22174	4.196274	-1.73568
H58	0.386345	4.84214	-1.41051
C59	1.712061	-0.09429	1.959208
H60	2.363208	0.367061	2.712848
H61	0.912513	-0.61098	2.489306
H62	2.312118	-0.85018	1.440612

Table S387. Rh^I(bisq^{Me4})(κ¹-TFA) thermodynamic values

Temp	298.15	498.15
E _{gas}	-1826.06	-1826.06
E _{solv}	-1826.07	-1826.07
G	-1825.65	-1825.71
ZPE	296.964	296.964
H _{vib}	19.609	51.510
S _{trans}	45.079	47.629
S _{rot}	37.097	38.627
S _{vib}	126.813	207.210

solv	-10.0	-10.0
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Table S388. Rh^I(bisq^{Me4})(κ²-TFA) Cartesian coordinates

Atom	x	y	z
Rh1	-1.38185	0.507447	-2.04781
N2	-2.199	-0.6153	-0.51144
C3	-2.97351	-1.63224	-0.89135
C4	-3.74719	-2.39996	-0.00102
C5	-3.71875	-2.09069	1.336567
C6	-5.50919	3.014522	-1.56752
C7	-5.28347	2.13707	-2.59975
C8	-4.01486	1.538797	-2.71629
N9	-3.00412	1.780569	-1.88016
H10	-2.98328	-1.83697	-1.95544
H11	-4.35638	-3.20962	-0.38884
H12	-4.31417	-2.64438	2.057834
H13	-3.80566	0.826285	-3.50569
O14	-0.21176	1.263998	-3.72225
C15	0.60694	0.324254	-3.51811
O16	0.40951	-0.57661	-2.65546
C17	1.885595	0.266774	-4.36987
F18	2.865063	-0.41125	-3.74253
F19	1.645057	-0.34996	-5.54507
F20	2.348297	1.502603	-4.64286
C21	-4.45377	3.33232	-0.67756
C22	-3.17317	2.714903	-0.87368
C23	-2.07769	3.102321	-0.03591
C24	-2.31986	4.014154	0.979524
C25	-3.59169	4.581389	1.206335
C26	-4.64083	4.254912	0.382757
H27	-1.48654	4.312908	1.608719
H28	-3.72823	5.288275	2.019739
H29	-5.62296	4.699838	0.519987
C30	-2.88715	-1.03851	1.792142
C31	-2.10001	-0.3138	0.835419
C32	-1.19744	0.696043	1.299536
C33	-1.16185	0.969822	2.657948
C34	-1.96878	0.289229	3.593879

C35	-2.81251	-0.70723	3.168802
H36	-0.46911	1.729188	3.008849
H37	-1.90481	0.546366	4.647348
H38	-3.42634	-1.2627	3.873124
H39	-6.05828	1.883394	-3.3156
H40	-6.47996	3.482058	-1.42506
C41	-0.66696	2.62544	-0.23134
C42	-0.24079	1.442257	0.413586
C43	1.099108	1.02882	0.324464
C44	2.010174	1.803687	-0.42531
C45	1.586915	2.981324	-1.06931
C46	0.243207	3.405574	-0.96679
C47	2.579697	3.76296	-1.90923
H48	2.133374	4.643397	-2.36961
H49	3.435004	4.105519	-1.31396
H50	2.977003	3.142064	-2.71952
C51	3.439092	1.323191	-0.58371
H52	4.136893	2.147522	-0.74343
H53	3.784652	0.766724	0.290442
H54	3.526612	0.651842	-1.44836
C55	-0.22155	4.645531	-1.70592
H56	-0.11032	4.513279	-2.78843
H57	-1.27107	4.866793	-1.51115
H58	0.356601	5.532788	-1.42268
C59	1.558562	-0.27545	0.942543
H60	2.345285	-0.12178	1.691733
H61	0.742051	-0.80619	1.432369
H62	1.967992	-0.93871	0.172498

Table S389. Rh^I(bisq^{Me4})(κ²-TFA) thermodynamic values

Temp	298.15	498.15
E_{gas}	-1826.06	-1826.06
E_{solv}	-1826.08	-1826.08
G	-1825.65	-1825.72
ZPE	297.466	297.466
H_{vib}	19.391	51.253
S_{trans}	45.079	47.629
S_{rot}	37.025	38.555

S_{vib}	124.571	204.871
solv	-12.1	-12.1

Table S390. Rh^I(bisq^{Me4})(Me) Cartesian coordinates

Atom	x	y	z
Rh1	-0.96291	0.7792	-1.85198
N2	-1.91677	-0.65546	-0.47648
C3	-2.59653	-1.74762	-0.79469
C4	-3.29476	-2.52674	0.154277
C5	-3.29197	-2.13992	1.475187
C6	-5.58111	2.471986	-1.69798
C7	-5.18665	1.625666	-2.70465
C8	-3.81405	1.336931	-2.84292
N9	-2.87565	1.805431	-2.02477
H10	-2.60123	-2.01686	-1.84789
H11	-3.83093	-3.41167	-0.17371
H12	-3.82909	-2.71119	2.227756
H13	-3.46514	0.70885	-3.65642
C14	-4.60915	3.039527	-0.83423
C15	-3.23164	2.676544	-1.01489
C16	-2.23746	3.266124	-0.15215
C17	-2.66697	4.159392	0.819806
C18	-4.02162	4.50618	0.996362
C19	-4.98097	3.951633	0.184432
H20	-1.91972	4.601335	1.472148
H21	-4.30011	5.205011	1.780257
H22	-6.03247	4.200007	0.305692
C23	-2.57563	-0.97768	1.860791
C24	-1.88294	-0.26189	0.83923
C25	-1.12351	0.89626	1.142239
C26	-1.08573	1.325886	2.457422
C27	-1.78411	0.638985	3.477484
C28	-2.51363	-0.49415	3.19211
H29	-0.50349	2.208555	2.706891
H30	-1.73705	1.010724	4.497449
H31	-3.04675	-1.0274	3.975023
H32	-5.89953	1.192932	-3.39956
H33	-6.62732	2.730702	-1.55649

C34	-0.77856	2.962346	-0.27322
C35	-0.35204	1.616342	0.055334
C36	1.032801	1.259173	-0.13185
C37	1.94585	2.255602	-0.55997
C38	1.516358	3.56454	-0.82853
C39	0.141304	3.918299	-0.70765
C40	-0.12984	1.902391	-3.34523
H41	0.758335	2.460765	-3.02916
H42	0.166242	1.14753	-4.09831
H43	-0.83437	2.601297	-3.81378
C44	2.54391	4.597849	-1.24867
H45	2.089292	5.532509	-1.57611
H46	3.22847	4.845366	-0.42471
H47	3.169579	4.237033	-2.07306
C48	3.418194	1.929861	-0.7176
H49	4.047791	2.653039	-0.18631
H50	3.67356	0.939991	-0.34027
H51	3.723241	1.965822	-1.77213
C52	-0.312	5.300314	-1.14209
H53	0.134713	6.092437	-0.528
H54	-0.02227	5.499679	-2.18063
H55	-1.39406	5.412793	-1.08101
C56	1.538648	-0.0848	0.368762
H57	2.181193	-0.57803	-0.36642
H58	2.125246	0.016734	1.293772
H59	0.717472	-0.76979	0.580997

Table S391. Rh^I(bisq^{Me4})(Me) thermodynamic values

Temp	298.15	498.15
E_{gas}	-1339.73	-1339.73
E_{solv}	-1339.74	-1339.74
G	-1339.30	-1339.35
ZPE	300.851	300.851
H_{vib}	16.510	44.953
S_{trans}	44.552	47.102
S_{rot}	35.994	37.524
S_{vib}	103.726	175.328
solv	-7.5	-7.5

Table S392. Rh^I(bisq^{Me4})(Me)(TFAH) Cartesian coordinates

Atom	x	y	z
Rh1	-1.38354	0.475961	-2.26275
N2	-2.04376	-0.61428	-0.35678
C3	-2.80804	-1.63834	-0.71982
C4	-3.60813	-2.38288	0.171035
C5	-3.60991	-2.03398	1.498976
C6	-5.41273	3.023521	-1.52423
C7	-5.17581	2.231273	-2.61876
C8	-3.88679	1.702298	-2.80992
N9	-2.86125	1.89935	-1.97149
H10	-2.79969	-1.87455	-1.77995
H11	-4.21045	-3.20308	-0.20621
H12	-4.22253	-2.56603	2.222632
H13	-3.67414	1.080372	-3.66859
O14	-0.08042	-1.20826	-2.61783
C15	1.10048	-0.91036	-2.77913
O16	1.574558	0.305543	-2.77007
C17	2.181513	-1.98002	-2.96625
F18	2.873105	-1.76771	-4.09647
F19	3.047131	-1.93008	-1.92932
F20	1.647678	-3.20197	-3.01139
H21	0.750834	0.889936	-2.59424
C22	-4.34844	3.309929	-0.63379
C23	-3.05323	2.738369	-0.8843
C24	-1.9765	3.081308	-0.00516
C25	-2.23405	3.928463	1.063316
C26	-3.5109	4.464099	1.322016
C27	-4.55282	4.160105	0.481383
H28	-1.40747	4.190847	1.717073
H29	-3.65955	5.118963	2.175804
H30	-5.5465	4.568205	0.647679
C31	-2.78445	-0.97215	1.943589
C32	-1.98012	-0.27894	0.975647
C33	-1.08444	0.742361	1.4303
C34	-1.05897	1.042867	2.783208
C35	-1.88076	0.389117	3.725431

C36	-2.72839	-0.60883	3.31253
H37	-0.36794	1.807741	3.126064
H38	-1.8269	0.670438	4.773273
H39	-3.35669	-1.14195	4.021767
H40	-5.95335	2.001939	-3.3402
H41	-6.39342	3.450633	-1.33216
C42	-0.5553	2.621572	-0.16263
C43	-0.12316	1.481931	0.545554
C44	1.234333	1.11563	0.533781
C45	2.163654	1.91851	-0.16037
C46	1.734073	3.05878	-0.86488
C47	0.36825	3.417125	-0.8672
C52	-0.96497	1.255179	-4.14354
H53	-0.30537	2.138083	-4.1389
H54	-0.49977	0.50255	-4.79783
H55	-1.89442	1.574315	-4.63729
C55	2.746627	3.882449	-1.6402
H56	2.277261	4.669462	-2.22931
H57	3.472203	4.365119	-0.9731
H58	3.31815	3.256853	-2.33449
C58	3.619023	1.498997	-0.1738
H59	4.283697	2.303327	-0.48991
H60	3.952928	1.168167	0.814642
H61	3.771719	0.656516	-0.8613
C61	-0.10233	4.632306	-1.6425
H62	0.440346	5.538647	-1.3507
H63	0.047793	4.493677	-2.71982
H64	-1.16393	4.823265	-1.48727
C64	1.713333	-0.15149	1.213916
H65	2.269972	-0.78241	0.510894
H66	2.391294	0.060622	2.050823
H67	0.88536	-0.74244	1.605785

Table S393. Rh^I(bisq^{Me4})(Me)(TFAH) thermodynamic values

Temp	298.15	498.15
E_{gas}	-1866.52	-1866.52
E_{solv}	-1866.53	-1866.53
G	-1866.06	-1866.13

ZPE	326.576	326.576
H_{vib}	21.190	55.487
S_{trans}	45.157	47.707
S_{rot}	37.252	38.782
S_{vib}	136.993	223.445
solv	-8.9	-8.9

Table S394. Rh^{II}(bisq^{Me4})(TFA)₂ Cartesian coordinates

Atom	x	y	z
Rh1	-0.90234	0.763403	-1.97492
N2	-1.74867	-0.61678	-0.62333
C3	-2.3458	-1.68691	-1.13791
C4	-3.17365	-2.53709	-0.37669
C5	-3.38754	-2.24682	0.94875
C6	-5.29879	2.884906	-1.70238
C7	-4.97697	1.997875	-2.69991
C8	-3.66505	1.487314	-2.76051
N9	-2.7168	1.829263	-1.894
H10	-2.13835	-1.88087	-2.18575
H11	-3.63364	-3.39482	-0.85511
H12	-4.03875	-2.86507	1.561256
H13	-3.35938	0.801677	-3.54386
O14	0.886776	-0.26412	-2.07275
C15	0.854232	-1.38912	-2.69081
O16	-0.09924	-1.95868	-3.21489
C17	2.24157	-2.08128	-2.67438
F18	2.485005	-2.5802	-1.43258
F19	2.310235	-3.09936	-3.53988
F20	3.242648	-1.22224	-2.95955
O21	-0.12807	2.08102	-3.37732
C22	-0.62437	1.838466	-4.53544
O23	-1.46631	0.991179	-4.83485
C24	-0.04261	2.769288	-5.62648
F25	-0.65481	2.603084	-6.8065
F26	-0.18695	4.069321	-5.26925
F27	1.273878	2.54062	-5.80194
C29	-4.30631	3.295046	-0.77785
C30	-2.98729	2.752936	-0.90786

C31	-1.95426	3.189661	-0.02278
C32	-2.28163	4.107605	0.961563
C33	-3.58743	4.622332	1.111716
C34	-4.58393	4.227622	0.252478
H35	-1.49566	4.45073	1.628157
H36	-3.79384	5.33933	1.900741
H37	-5.59088	4.625287	0.340722
C38	-2.7381	-1.13414	1.539396
C39	-1.88209	-0.3339	0.718106
C40	-1.14816	0.74429	1.299223
C41	-1.33812	1.015465	2.643433
C42	-2.2194	0.259201	3.447474
C43	-2.9007	-0.8056	2.908769
H44	-0.77244	1.826304	3.093003
H45	-2.33876	0.513324	4.496538
H46	-3.56206	-1.4147	3.518967
H47	-5.70464	1.676892	-3.43718
H48	-6.30331	3.290389	-1.61358
C49	-0.52766	2.729263	-0.13811
C50	-0.13328	1.535311	0.522173
C51	1.22328	1.150518	0.543513
C52	2.17191	1.949526	-0.12019
C53	1.782631	3.138341	-0.77419
C54	0.434685	3.544488	-0.77608
C55	2.821608	3.93802	-1.53407
H56	2.402828	4.826727	-2.00278
H57	3.639784	4.263791	-0.88122
H58	3.264674	3.331098	-2.33144
C59	3.598115	1.452877	-0.20756
H60	4.300176	2.232152	-0.50275
H61	3.946001	1.036444	0.742135
H62	3.658259	0.649715	-0.95375
C63	0.005538	4.782994	-1.53578
H64	0.577564	5.667369	-1.23565
H65	0.151195	4.62996	-2.61022
H66	-1.04918	5.010147	-1.37903
C67	1.654655	-0.15062	1.18185
H68	2.450451	0.003022	1.919444
H69	0.830958	-0.65251	1.690085
H70	2.041214	-0.83393	0.418409

Table S395. Rh^{II}(bisq^{Me4})(TFA)₂ thermodynamic values

Temp	298.15	498.15
E_{gas}	-2352.26	-2352.26
E_{solv}	-2352.29	-2352.29
G	-2351.83	-2351.91
ZPE	316.442	316.442
H_{vib}	23.850	61.222
S_{trans}	45.590	48.140
S_{rot}	37.906	39.436
S_{vib}	155.721	250.004
solv	-18.8	-18.8

Table S396. [Rh^{II}(bisq^{Me4})(TFA)(TFAH)]⁺ Cartesian coordinates

Atom	x	y	z
Rh1	-1.15085	0.676886	-1.49952
N2	-2.04996	-0.60527	-0.1389
C3	-2.63259	-1.69092	-0.63723
C4	-3.37568	-2.59091	0.146318
C5	-3.52271	-2.32826	1.488602
C6	-5.56011	2.619263	-1.82582
C7	-5.03197	1.825881	-2.81812
C8	-3.70575	1.378111	-2.68707
N9	-2.93006	1.708573	-1.65913
H10	-2.51233	-1.85721	-1.70365
H11	-3.82306	-3.46104	-0.32046
H12	-4.10506	-2.98843	2.125283
H13	-3.2654	0.725222	-3.43471
O14	0.399905	-0.79094	-1.50757
C15	1.634851	-0.85889	-1.61261
O16	2.468151	0.060861	-1.90611
C17	2.310055	-2.22595	-1.34609
F18	3.005319	-2.60887	-2.4213
F19	3.151755	-2.10499	-0.30348
F20	1.401294	-3.16066	-1.05763
O21	-0.56434	1.851402	-3.12138

C22	0.559121	2.349932	-3.41232
O23	1.680045	2.130489	-2.90861
C24	0.545177	3.410714	-4.54333
F25	0.926914	4.602238	-4.02824
F26	1.409114	3.072718	-5.50659
F27	-0.66807	3.55996	-5.08456
H28	2.03333	0.983071	-2.26091
C29	-3.39089	2.574241	-0.69379
C30	-4.75084	3.019452	-0.73459
C31	-5.23512	3.864822	0.295775
C32	-4.3933	4.27611	1.301507
C33	-3.03481	3.888065	1.292552
C34	-2.5117	3.055433	0.317587
H35	-6.27113	4.189236	0.264639
H36	-4.75814	4.926	2.090621
H37	-2.36939	4.275783	2.058408
C38	-2.12715	-0.33675	1.209193
C39	-2.89962	-1.19169	2.059355
C40	-3.00185	-0.88974	3.440734
C41	-2.34676	0.202671	3.957564
C42	-1.55193	1.014903	3.119106
C43	-1.42215	0.76955	1.761276
H44	-3.59464	-1.54014	4.077173
H45	-2.41961	0.436128	5.01509
H46	-1.00732	1.848958	3.552024
H47	-5.61324	1.524834	-3.6822
H48	-6.59083	2.959594	-1.87354
C49	-1.03226	2.788297	0.293953
C50	-0.50175	1.645768	0.955769
C51	0.903857	1.481786	1.081573
C52	1.758822	2.471107	0.564257
C53	1.224496	3.625037	-0.06278
C54	-0.16441	3.777825	-0.22314
C55	2.145865	4.697668	-0.59881
H56	1.7237	5.695908	-0.46151
H57	3.123073	4.685312	-0.11725
H58	2.304922	4.557886	-1.67536
C59	3.262602	2.324662	0.671757
H60	3.741418	2.471207	-0.30146
H61	3.685088	3.073147	1.353147

H62	3.564412	1.345391	1.038986
C63	-0.70829	4.996308	-0.9402
H64	-0.19507	5.153187	-1.89266
H65	-1.77447	4.909984	-1.14799
H66	-0.5638	5.907645	-0.34693
C67	1.47164	0.267951	1.792625
H68	2.193696	-0.26857	1.170342
H69	2.00206	0.555113	2.70795
H70	0.694702	-0.44188	2.075607

Table S397. $[\text{Rh}^{\text{II}}(\text{bisq}^{\text{Me4}})(\text{TFA})(\text{TFAH})]^+$
thermodynamic values

Temp	298.15	498.15
E_{gas}	-2352.65	-2352.65
E_{solv}	-2352.71	-2352.71
G	-2352.25	-2352.32
ZPE	323.378	323.378
H_{vib}	23.835	61.365
S_{trans}	45.594	48.145
S_{rot}	37.962	39.492
S_{vib}	155.369	250.037
solv	-40.1	-40.1

Table S398. $\text{Rh}^{\text{III}}(\text{bisq}^{\text{Me4}})(\text{Me}_{\text{ax}})(\text{H}_{\text{eq}})(\text{TFA}_{\text{eq}})$
Cartesian coordinates

Atom	x	y	z
Rh1	-1.61275	0.129616	-1.87223
N2	-2.00232	-1.24496	0.077821
C3	-2.45444	-2.46333	-0.16296
C4	-2.96871	-3.32639	0.829804
C5	-3.02278	-2.87723	2.125187
C6	-6.2908	1.503862	-1.32208
C7	-5.91661	0.692903	-2.36377
C8	-4.55318	0.383282	-2.53322
N9	-3.58846	0.839911	-1.74164
H10	-2.42184	-2.78913	-1.19752
H11	-3.31891	-4.31518	0.551932
H12	-3.42867	-3.49659	2.920621

H13	-4.24136	-0.27672	-3.33114
O14	0.290997	-0.63914	-1.91865
C15	1.210312	-0.235	-2.72325
O16	1.254077	0.721585	-3.48442
C17	2.447023	-1.17489	-2.63617
F18	3.370501	-0.88203	-3.56266
F19	3.056663	-1.06726	-1.4195
F20	2.105976	-2.47092	-2.79062
H21	-1.35544	0.997233	-3.10053
C22	-3.92353	1.721715	-0.73038
C23	-5.29486	2.050703	-0.4767
C24	-5.62403	2.923136	0.590251
C25	-4.62988	3.477586	1.35904
C26	-3.27846	3.190393	1.074022
C27	-2.89994	2.332389	0.054045
H28	-6.67042	3.14969	0.776096
H29	-4.87551	4.151275	2.174661
H30	-2.49973	3.666849	1.661824
C31	-1.98427	-0.7948	1.374667
C32	-2.52301	-1.58901	2.439966
C33	-2.52175	-1.09158	3.767164
C34	-1.97517	0.139026	4.040024
C35	-1.39843	0.899748	2.999982
C36	-1.38708	0.467665	1.68434
H37	-2.94456	-1.70558	4.558265
H38	-1.96437	0.523713	5.055742
H39	-0.9274	1.849542	3.237222
H40	-6.64286	0.270033	-3.04966
H41	-7.33424	1.747021	-1.1402
C42	-1.42903	2.143659	-0.20484
C43	-0.68252	1.298054	0.654612
C44	0.72302	1.301692	0.606324
C45	1.382934	2.178342	-0.27903
C46	0.650061	3.004738	-1.15331
C47	-0.75769	2.997754	-1.1169
C48	-2.0602	-1.28538	-3.29355
H49	-2.28223	-0.8357	-4.26627
H50	-1.18025	-1.92635	-3.3883
H51	-2.91925	-1.88766	-2.97089
C52	2.896761	2.171044	-0.30523

H53	3.309622	2.993544	-0.88735
H54	3.3119	2.238142	0.706504
H55	3.271993	1.238077	-0.74012
C56	1.386206	3.854654	-2.16796
H57	0.711391	4.452057	-2.7788
H58	2.089468	4.545193	-1.68929
H59	1.950545	3.206283	-2.84625
C60	-1.54808	3.911259	-2.03187
H61	-1.25771	4.959391	-1.89936
H62	-1.37765	3.650449	-3.08128
H63	-2.61965	3.843938	-1.84624
C64	1.543911	0.339068	1.437378
H65	2.157453	-0.2864	0.781407
H66	2.224905	0.863353	2.118872
H67	0.920454	-0.32205	2.038111

Table S399. Rh^{III}(bisq^{Me4})(Me_{ax})(H_{eq})(TFA_{eq})
thermodynamic values

Temp	298.15	498.15
E _{gas}	-1866.54	-1866.54
E _{solv}	-1866.57	-1866.57
G	-1866.09	-1866.16
ZPE	326.827	326.827
H _{vib}	20.297	54.121
S _{trans}	45.157	47.707
S _{rot}	37.179	38.709
S _{vib}	133.700	219.947
solv	-14.5	-14.5

Table S400. Rh^{III}(bisq^{Me4})(Me_{eq})(H_{ax})(TFA_{eq})
Cartesian coordinates

Atom	x	y	z
Rh1	-1.50408	0.306775	-1.86492
N2	-1.66294	-1.17999	-0.09187
C3	-1.88989	-2.44876	-0.40108
C4	-2.42401	-3.38013	0.518592
C5	-2.74172	-2.95789	1.786616
C6	-6.25009	1.249762	-1.10562

C7	-5.82399	0.312118	-2.01207
C8	-4.44162	0.133054	-2.20542
N9	-3.50686	0.820993	-1.55191
H10	-1.62276	-2.73639	-1.41382
H11	-2.58573	-4.40618	0.204554
H12	-3.17855	-3.63824	2.513191
H13	-1.8862	-0.76402	-2.86266
H14	-4.07607	-0.60183	-2.91122
O15	0.481514	-0.13627	-2.16785
C16	0.870767	-1.31106	-2.50432
O17	0.234892	-2.33634	-2.7302
C18	2.421902	-1.38538	-2.55612
F19	2.856695	-2.43133	-3.27168
F20	2.982817	-0.27076	-3.07422
F21	2.917538	-1.52409	-1.29434
C22	-3.90081	1.792959	-0.64901
C23	-5.2952	2.022996	-0.40168
C24	-5.69753	3.014777	0.527088
C25	-4.75593	3.766892	1.184805
C26	-3.38585	3.548816	0.932351
C27	-2.93262	2.587997	0.041917
H28	-6.75943	3.16679	0.700201
H29	-5.0572	4.530499	1.895779
H30	-2.64842	4.155757	1.44978
C31	-1.89391	-0.75134	1.189157
C32	-2.47462	-1.61846	2.167709
C33	-2.73656	-1.12726	3.471678
C34	-2.4006	0.164428	3.800728
C35	-1.77316	1.000129	2.848701
C36	-1.51139	0.574086	1.558515
H37	-3.19062	-1.79105	4.20306
H38	-2.59388	0.543592	4.800111
H39	-1.46793	2.000829	3.14088
H40	-6.52095	-0.29522	-2.57944
H41	-7.30759	1.417378	-0.92007
C42	-1.44558	2.449049	-0.13796
C43	-0.75419	1.470564	0.618654
C44	0.653894	1.415381	0.588487
C45	1.364856	2.348168	-0.18906
C46	0.682021	3.341559	-0.92057

C47	-0.72473	3.402877	-0.89515
C48	-1.40053	1.479299	-3.55608
H49	-1.28719	0.862247	-4.45254
H50	-2.28654	2.114564	-3.6702
H51	-0.50592	2.101546	-3.44925
C52	2.870692	2.224693	-0.27901
H53	3.348711	3.142616	-0.62154
H54	3.316785	1.961134	0.683849
H55	3.136117	1.428216	-0.98568
C56	1.479691	4.317988	-1.76416
H57	0.845076	5.01417	-2.31065
H58	2.163879	4.915257	-1.14947
H59	2.092785	3.787838	-2.50142
C60	-1.45912	4.462117	-1.69386
H61	-1.22659	4.380258	-2.76055
H62	-2.54028	4.371362	-1.59129
H63	-1.18206	5.473638	-1.3739
C64	1.40932	0.334779	1.330669
H65	1.96457	-0.28949	0.623151
H66	2.136847	0.757807	2.033424
H67	0.745575	-0.31487	1.900662

Table S401. Rh^{III}(bisq^{Me4})(Me_{eq})(H_{ax})(TFA_{eq})
thermodynamic values

Temp	298.15	498.15
E_{gas}	-1866.55	-1866.55
E_{solv}	-1866.57	-1866.57
G	-1866.10	-1866.17
ZPE	326.595	326.595
H_{vib}	20.941	55.189
S_{trans}	45.157	47.707
S_{rot}	37.163	38.693
S_{vib}	134.428	220.745
solv	-14.2	-14.2

Table S402. Rh^{III}(bisq^{Me4})(Me_{eq})(H_{eq})(TFA_{ax})
Cartesian coordinates

Atom	x	y	z
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Rh1	-1.46215	0.291766	-2.01632
N2	-2.17756	-1.13293	-0.41319
C3	-2.81005	-2.26229	-0.68337
C4	-3.30652	-3.12081	0.324148
C5	-3.1358	-2.77387	1.642528
C6	-6.33401	1.549807	-1.4289
C7	-5.93954	0.799624	-2.51028
C8	-4.55808	0.589166	-2.73107
N9	-3.62147	1.109432	-1.95811
H10	-2.93061	-2.49599	-1.73687
H11	-3.81458	-4.03664	0.040151
H12	-3.50755	-3.40838	2.442703
O13	-2.13947	-1.06134	-3.37555
H14	-4.20166	-0.04887	-3.53583
H15	-0.053	-0.30962	-2.08333
C16	-1.41182	-1.82458	-4.12962
O17	-0.20647	-1.91939	-4.25512
C18	-2.34734	-2.76983	-4.93553
F19	-1.67602	-3.5178	-5.81757
F20	-2.9971	-3.61711	-4.09108
F21	-3.29629	-2.08228	-5.61138
C22	-3.98134	1.892881	-0.89647
C23	-5.3552	2.121925	-0.57533
C24	-5.68363	2.900893	0.562271
C25	-4.68415	3.439752	1.338389
C26	-3.32727	3.240868	0.995363
C27	-2.95488	2.487484	-0.1043
H28	-6.73021	3.064904	0.805706
H29	-4.93114	4.034688	2.212887
H30	-2.55361	3.703558	1.601525
C31	-1.98185	-0.766	0.889691
C32	-2.45854	-1.57133	1.969714
C33	-2.22993	-1.15061	3.303659
C34	-1.54413	0.017298	3.546101
C35	-1.0636	0.801211	2.472268
C36	-1.27111	0.437879	1.152239
H37	-2.59575	-1.76459	4.121856
H38	-1.36163	0.342812	4.566258
H39	-0.51061	1.71199	2.686408
H40	-6.66273	0.351175	-3.18377

H41	-7.38697	1.71375	-1.21327
C42	-1.49796	2.378066	-0.47118
C43	-0.70816	1.315015	0.05802
C44	0.717291	1.361475	-0.08527
C45	1.315893	2.469393	-0.68394
C46	0.521686	3.528159	-1.20046
C47	-0.87379	3.483594	-1.11363
C48	-0.79419	1.451409	-3.58543
H49	-0.50297	0.796146	-4.40864
H50	-1.60852	2.111817	-3.90754
H51	0.069104	2.053095	-3.28666
C52	2.821611	2.539961	-0.82728
H53	3.198997	3.548676	-0.63758
H54	3.333537	1.865062	-0.14093
H55	3.132954	2.266931	-1.84475
C56	1.219452	4.692726	-1.87318
H57	0.525609	5.353415	-2.39092
H58	1.771596	5.301652	-1.14527
H59	1.949619	4.342793	-2.61025
C60	-1.71554	4.584949	-1.72739
H61	-1.55642	4.631957	-2.81099
H62	-2.78044	4.423495	-1.56345
H63	-1.46642	5.570185	-1.3171
C64	1.554446	0.202784	0.417124
H65	2.247682	-0.13684	-0.35786
H66	2.15039	0.477776	1.296763
H67	0.932761	-0.6492	0.691741

Table S403. Rh^{III}(bisq^{Me4})(Me_{eq})(H_{eq})(TFA_{ax})
thermodynamic values

Temp	298.15	498.15
E_{gas}	-1866.53	-1866.53
E_{solv}	-1866.56	-1866.56
G	-1866.08	-1866.15
ZPE	326.210	326.210
H_{vib}	21.079	55.351
S_{trans}	45.157	47.707
S_{rot}	37.317	38.847
S_{vib}	136.230	222.611

solv	-14.5	-14.5
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Table S404. Rh^{III}(bisq^{Me4})(TFA)₃ Cartesian coordinates

Atom	x	y	z
Rh1	-1.60051	0.307144	-1.76901
N2	-2.25796	-0.95041	-0.21516
C3	-2.86659	-2.09671	-0.48424
C4	-3.30127	-2.97768	0.526701
C5	-3.08966	-2.64338	1.841459
C6	-6.3299	1.512613	-1.57831
C7	-5.81526	0.878846	-2.68234
C8	-4.42095	0.680839	-2.78189
N9	-3.57454	1.124017	-1.86024
H10	-3.00024	-2.32456	-1.53593
H11	-3.79105	-3.90298	0.243798
H12	-3.41372	-3.29794	2.646204
O13	-2.26309	-1.09396	-3.06216
H14	-3.9823	0.135918	-3.60633
O15	0.081103	-0.83469	-1.60401
C16	1.222821	-0.67904	-2.20375
O17	1.774412	0.313142	-2.63637
C18	1.987016	-2.03556	-2.20728
F19	3.003007	-2.02718	-3.07712
F20	2.509172	-2.25386	-0.96948
F21	1.195234	-3.08402	-2.49743
O22	-0.83539	1.58132	-3.15543
C23	-1.33039	1.768208	-4.331
O24	-2.33906	1.3146	-4.85236
C25	-0.49194	2.810397	-5.12463
F26	-0.60618	2.626757	-6.44436
F27	-0.96479	4.061584	-4.84505
F28	0.812523	2.801998	-4.80935
C29	-1.59577	-1.54844	-4.09294
O30	-0.49051	-1.28878	-4.50563
C31	-2.5004	-2.58209	-4.82511
F32	-1.86829	-3.15366	-5.84944
F33	-2.89322	-3.5638	-3.97445
F34	-3.62095	-1.98962	-5.29496

C35	-4.04643	1.862312	-0.79968
C36	-5.44914	2.032096	-0.59603
C37	-5.90069	2.728367	0.553401
C38	-4.99409	3.26542	1.437744
C39	-3.60815	3.163922	1.182858
C40	-3.12096	2.486724	0.079161
H41	-6.96981	2.839129	0.712675
H42	-5.33848	3.798613	2.318716
H43	-2.9054	3.653317	1.850712
C44	-2.00258	-0.58987	1.087148
C45	-2.42687	-1.43262	2.161505
C46	-2.15936	-1.04549	3.49786
C47	-1.48692	0.125971	3.753924
C48	-1.05625	0.942701	2.686458
C49	-1.29686	0.613572	1.362693
H50	-2.48579	-1.69307	4.306854
H51	-1.2749	0.425453	4.775878
H52	-0.509	1.855463	2.90419
H53	-6.45427	0.495234	-3.47014
H54	-7.40207	1.637625	-1.4503
C55	-1.6596	2.519728	-0.2574
C56	-0.78274	1.534024	0.287761
C57	0.62733	1.680487	0.128476
C58	1.125791	2.761168	-0.60528
C59	0.242536	3.706752	-1.1864
C60	-1.14613	3.606804	-0.99794
C64	0.819601	4.809702	-2.04581
H65	0.051253	5.413217	-2.52394
H66	1.459071	5.48181	-1.461
H67	1.432659	4.378845	-2.84259
C67	2.616984	2.879213	-0.82026
H68	2.922602	3.889113	-1.09382
H69	3.178262	2.59418	0.073551
H70	2.910761	2.200223	-1.6305
C70	-2.07733	4.625587	-1.62308
H71	-1.80644	5.647122	-1.33597
H72	-2.02712	4.567683	-2.71495
H73	-3.11473	4.469811	-1.32842
C73	1.574646	0.674403	0.74299
H74	2.356614	0.396523	0.034239

H75	2.070693	1.086625	1.632042
H76	1.061572	-0.23959	1.038698

Table S405. Rh^{III}(bisq^{Me4})(TFA)₃ thermodynamic values

Temp	298.15	498.15
E_{gas}	-2878.41	-2878.41
E_{solv}	-2878.45	-2878.45
G	-2877.97	-2878.06
ZPE	335.143	335.143
H_{vib}	27.988	70.960
S_{trans}	46.026	48.577
S_{rot}	38.519	40.050
S_{vib}	183.309	291.813
solv	-21.3	-21.3

Table S406. [Rh^{III}(bisq^{Me4})(TFA)₂(TFAH_{eq})]⁺ Cartesian coordinates

Atom	x	y	z
Rh1	-1.16986	0.747574	-1.51131
N2	-2.237	-0.52444	-0.22916
C3	-3.0126	-1.44855	-0.79043
C4	-3.80886	-2.33321	-0.04238
C5	-3.79882	-2.24047	1.327611
C6	-5.4714	2.850191	-1.94005
C7	-4.92195	2.199153	-3.02083
C8	-3.62643	1.654638	-2.91608
N9	-2.90169	1.791454	-1.81173
H10	-2.98927	-1.49676	-1.87223
H11	-4.41323	-3.06629	-0.56442
H12	-4.40684	-2.90099	1.939237
H13	-3.18916	1.064014	-3.71138
O14	0.375194	-0.65163	-1.05861
C15	1.584622	-0.86502	-1.24079
O16	2.464863	-0.14082	-1.80477
C17	2.142831	-2.20627	-0.70222
F18	2.253704	-3.07751	-1.71014
F19	3.348661	-2.01795	-0.14922

F20	1.322786	-2.71798	0.22598
O21	-0.43602	2.03581	-2.97289
C22	0.733447	2.272385	-3.40603
O23	1.837063	1.890051	-2.99106
C24	0.738942	3.261298	-4.60601
F25	0.611771	4.528063	-4.13112
F26	1.874423	3.187139	-5.29269
F27	-0.28916	3.027908	-5.43146
H28	2.095216	0.737788	-2.28868
C29	-3.37455	2.521577	-0.74648
C30	-4.70566	3.02968	-0.76059
C31	-5.18355	3.706919	0.390152
C32	-4.35943	3.889701	1.477451
C33	-3.01609	3.449592	1.440823
C34	-2.50651	2.780463	0.342263
H35	-6.20067	4.086297	0.392919
H36	-4.72554	4.408614	2.357614
H37	-2.36066	3.673083	2.2774
C39	-2.17443	-0.41565	1.14515
C40	-2.97739	-1.2767	1.960026
C41	-2.92337	-1.1584	3.371399
C42	-2.09738	-0.23018	3.957645
C43	-1.29261	0.599959	3.151009
C44	-1.3099	0.527754	1.766341
H45	-3.5393	-1.81841	3.974263
H46	-2.05217	-0.13552	5.037777
H47	-0.63384	1.320474	3.62663
H49	-5.47168	2.065634	-3.94566
H50	-6.48446	3.240386	-1.98142
C51	-1.03066	2.493249	0.215798
C52	-0.42727	1.453807	0.994298
C53	0.973561	1.412737	1.175241
C54	1.763926	2.434468	0.616526
C55	1.182854	3.463573	-0.17294
C56	-0.20364	3.527659	-0.34263
O59	-1.70908	-0.42894	-3.06894
C60	-0.84575	-0.83859	-3.96821
O61	0.354015	-0.68027	-4.0142
C62	-1.61762	-1.6055	-5.07898
F63	-2.49686	-0.76886	-5.67491

F64	-0.7928	-2.08719	-6.00045
F65	-2.31858	-2.62606	-4.54292
C65	2.072143	4.506962	-0.81658
H66	1.613858	4.935834	-1.70717
H67	2.289129	5.331757	-0.12539
H68	3.026452	4.078412	-1.12619
C68	3.257297	2.439752	0.846527
H69	3.779147	1.956619	0.009288
H70	3.647036	3.456187	0.925247
H71	3.535612	1.907146	1.755709
C71	-0.81829	4.705425	-1.06413
H72	-0.62122	4.654057	-2.13822
H73	-1.89698	4.761945	-0.92828
H74	-0.39109	5.645456	-0.70226
C74	1.627735	0.274404	1.935967
H75	2.537019	-0.06557	1.433542
H76	1.923394	0.57437	2.9488
H77	0.964216	-0.58505	2.027385

Table S407. $[\text{Rh}^{\text{III}}(\text{bisq}^{\text{Me4}})(\text{TFA})_2(\text{TFAH}_{\text{eq}})]^+$
thermodynamic values

Temp	298.15	498.15
E_{gas}	-2878.81	-2878.81
E_{solv}	-2878.87	-2878.87
G	-2878.39	-2878.48
ZPE	342.606	342.606
H_{vib}	27.901	70.959
S_{trans}	46.030	48.580
S_{rot}	38.556	40.086
S_{vib}	182.976	291.675
solv	-40.9	-40.9

Table S408. $[\text{Rh}^{\text{III}}(\text{bisq}^{\text{Me4}})(\kappa^1\text{-TFA}_{\text{ax}})(\kappa^2\text{-TFA}_{\text{eq,eq}})]^+$
Cartesian coordinates

Atom	x	y	z
Rh1	-1.25735	0.500875	-1.96586
N2	-2.17485	-0.77323	-0.61175
C3	-2.87539	-1.83585	-0.99388

C4	-3.5933	-2.62588	-0.07459
C5	-3.59972	-2.27637	1.255783
C6	-5.52086	2.878239	-1.59202
C7	-5.32722	1.882237	-2.51767
C8	-4.06449	1.2689	-2.60999
N9	-3.02922	1.632458	-1.85651
H10	-2.88113	-2.0513	-2.0557
H11	-4.14078	-3.48719	-0.44037
H12	-4.16497	-2.8542	1.981636
H13	-3.88708	0.457887	-3.30526
O14	-0.02819	1.47583	-3.38928
C15	0.768578	0.48857	-3.34078
O16	0.586305	-0.41406	-2.46369
C17	1.996783	0.436783	-4.26331
F18	3.012528	1.092696	-3.63703
F19	2.38314	-0.81587	-4.47863
F20	1.7567	1.050732	-5.41624
C21	-4.43947	3.301593	-0.78239
C22	-3.16743	2.669585	-0.95579
C23	-2.04509	3.137501	-0.22329
C24	-2.2282	4.164504	0.688707
C25	-3.48974	4.758992	0.901491
C26	-4.5762	4.343336	0.169017
H27	-1.36952	4.531451	1.242935
H28	-3.58945	5.557716	1.62934
H29	-5.54811	4.810858	0.29563
C30	-2.85106	-1.15522	1.69275
C31	-2.10955	-0.42379	0.717709
C32	-1.26975	0.649901	1.101162
C33	-1.23484	1.01034	2.437395
C34	-2.00443	0.329421	3.40785
C35	-2.78795	-0.74319	3.047726
H36	-0.58167	1.819764	2.750573
H37	-1.95218	0.64367	4.445378
H38	-3.35619	-1.29364	3.791792
H39	-6.12376	1.541763	-3.16954
H40	-6.48957	3.356014	-1.47601
C41	-0.66971	2.589191	-0.43979
C42	-0.34059	1.305566	0.109467
C43	1.031664	0.876029	0.118968

C44	2.016317	1.719455	-0.39758
C45	1.661447	2.962919	-0.99668
C46	0.323774	3.395699	-1.03837
O51	-2.13626	-0.59382	-3.44555
C52	-1.63933	-1.0011	-4.5868
O53	-0.55343	-0.81533	-5.09042
C54	-2.72127	-1.85478	-5.3106
F55	-3.05701	-2.91692	-4.54196
F56	-3.84039	-1.12072	-5.5017
F57	-2.29331	-2.29677	-6.48531
C57	2.759794	3.801538	-1.60528
H58	2.383977	4.681363	-2.12288
H59	3.462016	4.143897	-0.83582
H60	3.337509	3.211842	-2.32356
C60	3.472821	1.311252	-0.35506
H61	4.117915	2.155796	-0.10044
H62	3.661615	0.523756	0.373583
H63	3.798517	0.941733	-1.33427
C63	-0.04217	4.684616	-1.74568
H64	0.265774	4.64093	-2.7955
H65	-1.11541	4.86918	-1.72951
H66	0.449133	5.553478	-1.2948
C66	1.401188	-0.47465	0.68699
H67	1.990286	-1.04283	-0.03836
H68	2.003533	-0.37655	1.597668
H69	0.524516	-1.07022	0.938294

Table S409. $[\text{Rh}^{\text{III}}(\text{bisq}^{\text{Me4}})(\kappa^1\text{-TFA}_{\text{ax}})(\kappa^2\text{-TFA}_{\text{eq,eq}})]^+$ thermodynamic values

Temp	298.15	498.15
E _{gas}	-2352.02	-2352.02
E _{solv}	-2352.09	-2352.09
G	-2351.63	-2351.71
ZPE	317.836	317.836
H _{vib}	23.184	60.417
S _{trans}	45.590	48.140
S _{rot}	37.875	39.405
S _{vib}	149.352	243.278
solv	-40.5	-40.5

Table S410. $[\text{Rh}^{\text{III}}(\text{bisq}^{\text{Me4}})(\kappa^1\text{-TFA}_{\text{eq}})(\kappa^2\text{-TFA}_{\text{ax,eq}})]^+$ Cartesian coordinates

Atom	x	y	z
Rh1	-1.2698	0.69042	-1.93945
N2	-2.30067	-0.47336	-0.50206
C3	-3.22195	-1.33007	-0.93641
C4	-4.03148	-2.08701	-0.07052
C5	-3.8789	-1.93248	1.287104
C6	-5.49559	2.964301	-1.83623
C7	-5.18148	2.155364	-2.90488
C8	-3.90338	1.565132	-2.9761
N9	-2.98425	1.791873	-2.0456
H10	-3.31779	-1.42782	-2.01168
H11	-4.75899	-2.77232	-0.49047
H12	-4.49141	-2.49488	1.986147
H13	-3.60472	0.926721	-3.79895
O14	0.284695	-0.81697	-2.12853
C15	-0.40435	-1.35398	-3.03505
O16	-1.53566	-0.85198	-3.35204
C17	0.057982	-2.64443	-3.73175
F18	-0.56011	-3.6857	-3.14199
F19	-0.27287	-2.62115	-5.02414
F20	1.376282	-2.79664	-3.60943
O21	-0.19476	1.695664	-3.34843
C22	-0.67321	1.912873	-4.53998
O23	-1.79355	1.717282	-4.97373
C24	0.428063	2.517395	-5.45641
F25	-0.02381	2.71828	-6.69134
F26	0.84365	3.714819	-4.9617
F27	1.50111	1.709426	-5.5124
C29	-4.52342	3.230076	-0.8386
C30	-3.23894	2.634351	-0.98952
C31	-2.18928	2.909244	-0.07955
C32	-2.45877	3.730126	1.000455
C33	-3.74353	4.290165	1.195089
C34	-4.75396	4.059622	0.288524
H35	-1.66321	3.968868	1.70044
H36	-3.92017	4.92657	2.056361

H37	-5.73229	4.51282	0.418308
C38	-2.90556	-1.0343	1.788036
C39	-2.10629	-0.30646	0.851681
C40	-1.09469	0.574648	1.319911
C41	-0.91853	0.71715	2.687117
C42	-1.71681	0.016611	3.617018
C43	-2.69177	-0.84746	3.17717
H44	-0.14057	1.38285	3.049141
H45	-1.54853	0.159231	4.679634
H46	-3.30359	-1.40387	3.880812
H47	-5.89726	1.951054	-3.69295
H48	-6.48139	3.412114	-1.75028
C49	-0.79594	2.415347	-0.38506
C50	-0.21822	1.339147	0.381045
C51	1.160239	1.070682	0.31382
C52	1.989713	1.939361	-0.43268
C53	1.45726	3.077022	-1.0955
C54	0.081309	3.313707	-1.09178
C57	2.360938	4.019881	-1.85816
H58	2.080477	5.063191	-1.69006
H59	3.40877	3.915737	-1.5812
H60	2.276716	3.835316	-2.93567
C60	3.468809	1.659982	-0.54781
H61	3.78095	1.664477	-1.59714
H62	4.053488	2.436165	-0.03899
H63	3.75331	0.701141	-0.1209
C63	-0.46899	4.505438	-1.83277
H64	-0.09177	4.521399	-2.85808
H65	-1.557	4.513201	-1.87022
H66	-0.1501	5.440799	-1.35575
C66	1.749806	-0.15676	0.978884
H67	2.208819	-0.80892	0.229257
H68	2.524006	0.105015	1.707749
H69	0.993137	-0.74318	1.497324

Table S411. $[\text{Rh}^{\text{III}}(\text{bisq}^{\text{Me4}})(\kappa^1\text{-TFA}_{\text{eq}})(\kappa^2\text{-TFA}_{\text{ax,eq}})]^+$ thermodynamic values

Temp	298.15	498.15
E_{gas}	-2352.02	-2352.02

E_{solv}	-2352.09	-2352.09
G	-2351.63	-2351.71
ZPE	317.634	317.634
H_{vib}	23.321	60.576
S_{trans}	45.590	48.140
S_{rot}	37.823	39.353
S_{vib}	150.264	244.241
solv	-41.7	-41.7

Table S412.

$[\text{Rh}^{\text{III}}(\text{bisq}^{\text{Me4}})(\text{Me}_{\text{ax}})(\text{TFA}_{\text{eq}})(\text{TFAH}_{\text{eq}})]^+$ Cartesian coordinates

Atom	x	y	z
Rh1	-1.15933	0.511042	-1.51142
N2	-1.80189	-0.93521	-0.14943
C3	-2.02541	-2.19503	-0.5072
C4	-2.75125	-3.09857	0.29063
C5	-3.29171	-2.65199	1.473786
C6	-5.61841	2.513862	-1.41383
C7	-5.35714	1.355902	-2.10144
C8	-4.05525	0.833634	-2.06591
N9	-3.04603	1.396164	-1.40394
H10	-1.63822	-2.5029	-1.46976
H11	-2.89922	-4.11364	-0.06004
H12	-3.90764	-3.30276	2.087484
H13	-3.83567	-0.07331	-2.60814
O14	0.623029	-0.64681	-1.47585
C15	1.843036	-0.56618	-1.69963
O16	2.507885	0.374982	-2.23505
C17	2.704351	-1.79407	-1.31285
F18	2.970435	-2.50939	-2.41381
F19	3.854852	-1.40331	-0.75366
F20	2.04895	-2.57591	-0.44121
O21	-0.82699	2.036972	-2.90018
C22	0.201611	2.537729	-3.43161
O23	1.407327	2.252742	-3.28601
C24	-0.10409	3.668961	-4.449
F25	-1.25562	4.293982	-4.15562
F26	0.879237	4.577185	-4.46129

F27	-0.21328	3.132427	-5.67628
H28	1.921506	1.204238	-2.64159
C29	-3.27226	2.554899	-0.67715
C30	-4.58499	3.138522	-0.67871
C31	-4.83938	4.323728	0.055253
C32	-3.83636	4.91388	0.782624
C33	-2.55297	4.333674	0.792329
C34	-2.24085	3.181395	0.084611
H35	-5.83908	4.746886	0.029857
H36	-4.02257	5.81918	1.351417
H37	-1.76834	4.803595	1.377616
C38	-2.188	-0.50518	1.103558
C39	-3.01627	-1.33604	1.919544
C40	-3.49242	-0.8339	3.15736
C41	-3.11615	0.417385	3.585067
C42	-2.20427	1.181991	2.8233
C43	-1.71839	0.742447	1.603527
H44	-4.13793	-1.461	3.764446
H45	-3.47654	0.803719	4.533134
H46	-1.838	2.12287	3.222841
H47	-6.11913	0.838503	-2.67311
H48	-6.60877	2.959989	-1.41784
C49	-0.8382	2.669021	0.201666
C50	-0.58978	1.482255	0.936478
C51	0.745777	1.095436	1.234648
C52	1.811251	1.891114	0.779061
C53	1.556694	3.098687	0.085492
C54	0.241238	3.481097	-0.22669
C59	-1.60646	-0.57838	-3.20632
H60	-1.95285	0.134232	-3.95488
H61	-0.67617	-1.05127	-3.52503
H62	-2.3638	-1.33763	-3.00386
C62	2.707162	3.985111	-0.34065
H63	2.436707	5.042129	-0.30092
H64	3.585073	3.850237	0.291253
H65	3.004589	3.765952	-1.3745
C65	3.24479	1.463831	1.030436
H66	3.877782	1.676432	0.166114
H67	3.677804	1.992034	1.889659
H68	3.329693	0.395676	1.228473

C68	-0.00288	4.745259	-1.02719
H69	0.73279	4.852191	-1.82797
H70	-0.99169	4.755447	-1.48462
H71	0.082909	5.644644	-0.40433
C71	1.028834	-0.14428	2.059897
H72	1.802796	0.046303	2.807859
H73	0.144118	-0.49138	2.592286
H74	1.378468	-0.9738	1.434538

Table S413.

$[\text{Rh}^{\text{III}}(\text{bisq}^{\text{Me4}})(\text{Me}_{\text{ax}})(\text{TFA}_{\text{eq}})(\text{TFAH}_{\text{eq}})]^+$
thermodynamic values

Temp	298.15	498.15
E_{gas}	-2392.53	-2392.53
E_{solv}	-2392.59	-2392.59
G	-2392.09	-2392.17
ZPE	347.661	347.661
H_{vib}	24.753	64.198
S_{trans}	45.656	48.206
S_{rot}	37.965	39.495
S_{vib}	159.773	259.272
solv	-38.4	-38.4

Table S414.

$[\text{Rh}^{\text{III}}(\text{bisq}^{\text{Me4}})(\text{Me}_{\text{eq}})(\text{TFA}_{\text{ax}})(\text{TFAH}_{\text{eq}})]^+$ Cartesian
coordinates

Atom	x	y	z
Rh1	-1.45641	0.317845	-1.96763
N2	-2.00845	-1.15051	-0.20369
C3	-2.62622	-2.27347	-0.54818
C4	-3.14638	-3.19778	0.380816
C5	-3.0314	-2.92175	1.72044
C6	-6.13536	1.465351	-1.5731
C7	-5.69448	0.779704	-2.67993
C8	-4.3197	0.50877	-2.82314
N9	-3.41719	0.914864	-1.93612
H10	-2.72607	-2.45654	-1.61214
H11	-3.63097	-4.09926	0.021997

H12	-3.42743	-3.6001	2.47125
O13	-2.07476	-1.20259	-3.24192
H14	-3.95533	-0.08156	-3.65167
O15	0.58815	-0.31101	-1.8187
C16	1.506047	-0.69624	-2.55768
O17	1.502681	-0.94583	-3.81062
C18	2.887412	-0.91135	-1.88894
F19	3.738184	-1.54484	-2.68797
F20	3.411082	0.290312	-1.56447
F21	2.732622	-1.61991	-0.76067
H22	0.55274	-1.03037	-4.26921
C23	-1.66259	-1.66419	-4.35484
O24	-0.5941	-1.47445	-4.95157
C25	-2.72132	-2.58206	-5.02182
F26	-2.26754	-3.14446	-6.13424
F27	-3.10022	-3.54727	-4.163
F28	-3.81405	-1.84209	-5.324
C29	-3.81469	1.660155	-0.84672
C30	-5.19773	1.928446	-0.6172
C31	-5.57113	2.656658	0.540371
C32	-4.60707	3.114095	1.408736
C33	-3.2394	2.886647	1.138704
C34	-2.82546	2.174051	0.026242
H35	-6.62392	2.851265	0.722167
H36	-4.88962	3.673281	2.295068
H37	-2.4925	3.296884	1.811349
C38	-1.85714	-0.85838	1.129747
C39	-2.38164	-1.7335	2.136446
C40	-2.2366	-1.40819	3.508136
C41	-1.58312	-0.25803	3.878728
C42	-1.04143	0.589356	2.890213
C43	-1.15608	0.317415	1.535083
H44	-2.64443	-2.08506	4.253498
H45	-1.46865	-0.00061	4.92695
H46	-0.50828	1.483683	3.199899
H47	-6.37989	0.421367	-3.43962
H48	-7.19271	1.665114	-1.42333
C49	-1.35379	2.057726	-0.29626
C50	-0.52179	1.272991	0.57625
C51	0.861648	1.496905	0.638551

C52	1.417884	2.575582	-0.09122
C53	0.621949	3.369131	-0.94888
C54	-0.75969	3.144169	-1.0332
C59	-1.04322	1.511385	-3.60931
H60	-0.95219	0.868177	-4.48416
H61	-1.85449	2.224042	-3.76205
H62	-0.10131	2.035555	-3.43562
C62	1.270929	4.506916	-1.7102
H63	0.662651	4.850993	-2.54568
H64	1.446107	5.373165	-1.05891
H65	2.243165	4.212876	-2.11392
C65	2.878399	2.928046	0.063768
H66	3.004861	4.00634	0.197481
H67	3.341988	2.430114	0.913251
H68	3.446897	2.649562	-0.83112
C68	-1.62715	4.121129	-1.79196
H69	-1.29617	4.237358	-2.8272
H70	-2.67505	3.828327	-1.80893
H71	-1.56835	5.112672	-1.32719
C71	1.765021	0.61017	1.474073
H72	2.668547	0.347663	0.922099
H73	2.081465	1.10407	2.400696
H74	1.268955	-0.31901	1.750763

Table S415.

$[\text{Rh}^{\text{III}}(\text{bisq}^{\text{Me4}})(\text{Me}_{\text{eq}})(\text{TFA}_{\text{ax}})(\text{TFAH}_{\text{eq}})]^{+}$
thermodynamic values

Temp	298.15	498.15
E_{gas}	-2392.52	-2392.52
E_{solv}	-2392.58	-2392.58
G	-2392.08	-2392.16
ZPE	347.840	347.840
H_{vib}	24.857	64.350
S_{trans}	45.656	48.206
S_{rot}	38.094	39.625
S_{vib}	160.526	260.151
solv	-37.1	-37.1

Table S416. Rh^{III}(bisq^{Me4})(Me_{ax})(TFA)₂ Cartesian coordinates

Atom	x	y	z
Rh1	-1.719	0.231736	-1.79855
N2	-2.40906	-0.91864	-0.12531
C3	-3.20742	-1.95682	-0.34744
C4	-3.68011	-2.81876	0.658609
C5	-3.29886	-2.58609	1.954218
C6	-6.37802	1.626677	-1.52384
C7	-5.88972	1.137859	-2.71062
C8	-4.50544	0.895103	-2.83734
N9	-3.64067	1.148798	-1.86139
H10	-3.4855	-2.13636	-1.37616
H11	-4.3222	-3.64916	0.386081
H12	-3.62546	-3.23167	2.76495
H13	-4.07837	0.49918	-3.75126
O14	0.094264	-0.69011	-1.54217
C15	0.892164	-1.0265	-2.50579
O16	0.775203	-0.94348	-3.71511
C17	2.224274	-1.60977	-1.9504
F18	2.746309	-2.51691	-2.78758
F19	3.142049	-0.61266	-1.8112
F20	2.09198	-2.19625	-0.74239
O21	-0.92913	1.444627	-3.23235
C22	-1.38908	1.642182	-4.41453
O23	-2.38814	1.20023	-4.97238
C24	-0.52929	2.683358	-5.18338
F25	-0.61886	2.517463	-6.50875
F26	-0.99167	3.934976	-4.89706
F27	0.772904	2.656945	-4.84712
C28	-4.07803	1.793369	-0.72236
C29	-5.47507	1.985754	-0.49121
C30	-5.90602	2.561131	0.731033
C31	-4.98269	2.981427	1.658709
C32	-3.60224	2.888678	1.374557
C33	-3.12943	2.320191	0.204131
H34	-6.97158	2.680595	0.907285
H35	-5.30825	3.426704	2.594137
H36	-2.88571	3.305113	2.076148

C37	-2.03612	-0.62761	1.175279
C38	-2.47089	-1.47737	2.248676
C39	-2.08442	-1.20097	3.5832
C40	-1.30509	-0.1061	3.86054
C41	-0.89801	0.740889	2.811376
C42	-1.23465	0.515928	1.484481
H43	-2.42081	-1.86823	4.371733
H44	-1.00533	0.117347	4.879923
H45	-0.29244	1.611588	3.042597
H46	-6.54292	0.902708	-3.54384
H47	-7.44411	1.77329	-1.37065
C48	-1.66596	2.401085	-0.13088
C49	-0.74575	1.513209	0.479058
C50	0.64284	1.684558	0.282867
C51	1.096273	2.733596	-0.53476
C52	0.182473	3.61605	-1.15034
C53	-1.19974	3.467357	-0.93724
C58	-2.17352	-1.26596	-3.13294
H59	-1.70708	-1.00946	-4.07827
H60	-1.74116	-2.18363	-2.72866
H61	-3.25751	-1.35961	-3.24388
C61	0.706435	4.699884	-2.07237
H62	-0.09147	5.269382	-2.5441
H63	1.349729	5.409226	-1.53788
H64	1.297831	4.259725	-2.88062
C64	2.585427	2.872734	-0.77456
H65	2.849189	3.823883	-1.23503
H66	3.151111	2.787847	0.158696
H67	2.941515	2.074131	-1.43731
C67	-2.17302	4.42735	-1.59163
H68	-2.15105	4.31442	-2.68063
H69	-3.19844	4.267624	-1.25915
H70	-1.91868	5.468603	-1.36742
C70	1.645621	0.737659	0.906973
H71	2.422969	0.4686	0.191739
H72	2.144767	1.194202	1.77302
H73	1.180335	-0.18982	1.23678

Table S417. Rh^{III}(bisq^{Me4})(Me_{ax})(TFA)₂ thermodynamic values

Temp	298.15	498.15
E _{gas}	-2392.13	-2392.13
E _{solv}	-2392.17	-2392.17
G	-2391.68	-2391.75
ZPE	340.758	340.758
H _{vib}	24.678	64.007
S _{trans}	45.652	48.202
S _{rot}	37.937	39.467
S _{vib}	159.112	258.342
solv	-20.1	-20.1

Table S418. Rh^{III}(bisq^{Me4})(Me_{eq})(TFA)₂ Cartesian coordinates

Atom	x	y	z
Rh1	-1.51188	0.359307	-1.95852
N2	-2.15868	-1.0363	-0.12251
C3	-2.81547	-2.14674	-0.41324
C4	-3.34615	-3.02077	0.561665
C5	-3.18819	-2.70534	1.887289
C6	-6.22347	1.530864	-1.52656
C7	-5.77976	0.840225	-2.62769
C8	-4.39869	0.593342	-2.77656
N9	-3.49726	1.027794	-1.90446
H10	-2.92432	-2.37613	-1.46439
H11	-3.86368	-3.92038	0.24552
H12	-3.58339	-3.34662	2.671312
O13	-2.12337	-0.91732	-3.41956
H14	-4.01039	-0.01012	-3.59021
O15	0.415627	-0.31038	-1.81803
C16	1.133826	-0.79668	-2.77668
O17	0.935326	-0.85899	-3.97755
C18	2.474453	-1.34598	-2.20856
F19	3.150218	-2.05863	-3.115
F20	3.284354	-0.3128	-1.82403
F21	2.291619	-2.11928	-1.12006
C22	-1.70379	-2.1303	-3.62914
O23	-1.10387	-2.89725	-2.90182
C24	-2.17166	-2.5827	-5.04065
F25	-1.81069	-3.84376	-5.30098

F26	-3.52959	-2.51949	-5.11826
F27	-1.67621	-1.79132	-6.00588
C28	-3.89792	1.786167	-0.82741
C29	-5.2854	2.027643	-0.58627
C30	-5.67231	2.757044	0.56593
C31	-4.71658	3.246125	1.425302
C32	-3.34574	3.049659	1.148337
C33	-2.91581	2.33906	0.041006
H34	-6.73003	2.924836	0.750446
H35	-5.00892	3.804079	2.309921
H36	-2.60285	3.481072	1.81246
C37	-1.9717	-0.70329	1.193198
C38	-2.49112	-1.52445	2.246168
C39	-2.29487	-1.15136	3.599095
C40	-1.59746	-0.00705	3.90323
C41	-1.06971	0.791644	2.866545
C42	-1.23746	0.473188	1.528618
H43	-2.69859	-1.78716	4.382978
H44	-1.44096	0.284777	4.937604
H45	-0.50405	1.683265	3.122177
H46	-6.46642	0.455652	-3.3742
H47	-7.28322	1.709528	-1.36385
C48	-1.43931	2.254881	-0.25731
C49	-0.61705	1.381226	0.511495
C50	0.786617	1.496077	0.461462
C51	1.364617	2.536927	-0.28688
C52	0.559978	3.435647	-1.02533
C53	-0.83705	3.306909	-1.01189
C58	-1.03329	1.537213	-3.57927
H59	-0.83123	0.845116	-4.39307
H60	-1.87822	2.192154	-3.81028
H61	-0.1403	2.116518	-3.33886
C61	2.871149	2.669666	-0.31264
H62	3.197267	3.676822	-0.57396
H63	3.312022	2.418128	0.655252
H64	3.296228	1.975239	-1.04734
C64	1.22638	4.529029	-1.83917
H65	0.521722	5.064141	-2.47407
H66	1.712913	5.271374	-1.19389
H67	2.001733	4.115715	-2.49243

C67	-1.69929	4.305889	-1.7554
H68	-1.48298	4.292648	-2.82841
H69	-2.7627	4.103056	-1.63513
H70	-1.5168	5.325871	-1.39781
C70	1.677341	0.49833	1.16963
H71	2.451695	0.1363	0.490621
H72	2.178035	0.940176	2.041257
H73	1.115322	-0.36875	1.513491

Table S419. $\text{Rh}^{\text{III}}(\text{bisq}^{\text{Me4}})(\text{Me}_{\text{eq}})(\text{TFA})_2$
thermodynamic values

Temp	298.15	498.15
E_{gas}	-2392.12	-2392.12
E_{solv}	-2392.15	-2392.15
G	-2391.66	-2391.74
ZPE	339.823	339.823
H_{vib}	25.164	64.589
S_{trans}	45.652	48.202
S_{rot}	38.032	39.562
S_{vib}	163.207	262.682
solv	-19.1	-19.1

Table S420. $[\text{Rh}^{\text{IV}}(\text{bisq}^{\text{Me4}})(\text{Me}_{\text{ax}})(\text{TFA})_2]^+$
Cartesian coordinates

Atom	x	y	z
Rh1	-1.73504	0.222809	-1.77106
N2	-2.44634	-0.91169	-0.12509
C3	-3.28341	-1.92665	-0.33845
C4	-3.76567	-2.77103	0.672672
C5	-3.35352	-2.54975	1.964048
C6	-6.38448	1.639599	-1.52302
C7	-5.90855	1.109755	-2.69977
C8	-4.53234	0.838071	-2.82129
N9	-3.65812	1.109051	-1.85409
H10	-3.58415	-2.09646	-1.36245
H11	-4.43632	-3.58219	0.413103
H12	-3.68357	-3.18963	2.777441
H13	-4.12329	0.401795	-3.7238

O14	0.084646	-0.64282	-1.51852
C15	0.913338	-0.87494	-2.49795
O16	0.79373	-0.63578	-3.68622
C17	2.245857	-1.50305	-2.00213
F18	2.729596	-2.36098	-2.89906
F19	3.160926	-0.51428	-1.827
F20	2.106259	-2.14146	-0.82794
O21	-0.94939	1.465867	-3.13273
C22	-1.34169	1.612903	-4.36922
O23	-2.31348	1.129778	-4.9223
C24	-0.44687	2.626551	-5.12781
F25	-0.52189	2.451338	-6.44329
F26	-0.89332	3.880598	-4.83898
F27	0.839849	2.55971	-4.7507
C28	-4.08202	1.783436	-0.72585
C29	-5.47475	2.00348	-0.49885
C30	-5.89416	2.604652	0.715742
C31	-4.96397	3.01399	1.642395
C32	-3.58503	2.88738	1.363349
C33	-3.12642	2.29787	0.196877
H34	-6.95642	2.748922	0.890253
H35	-5.28167	3.476038	2.571704
H36	-2.86307	3.295212	2.06484
C37	-2.0472	-0.62743	1.169494
C38	-2.48882	-1.46697	2.246229
C39	-2.06366	-1.2103	3.573886
C40	-1.23389	-0.14897	3.84189
C41	-0.81442	0.685826	2.78925
C42	-1.20105	0.485439	1.468921
H43	-2.40554	-1.86849	4.367072
H44	-0.9041	0.055382	4.855279
H45	-0.17459	1.533151	3.017078
H46	-6.56851	0.866269	-3.52473
H47	-7.44744	1.808344	-1.37387
C48	-1.66428	2.356732	-0.15004
C49	-0.739	1.491979	0.465252
C50	0.670516	1.678547	0.253376
C51	1.125495	2.738925	-0.5602
C52	0.204885	3.598828	-1.18328
C53	-1.19516	3.427745	-0.97162

C58	-2.12548	-1.30634	-3.10525
H59	-1.60148	-1.0683	-4.02473
H60	-1.72552	-2.21047	-2.64421
H61	-3.20085	-1.38239	-3.26963
C61	0.710107	4.699079	-2.08641
H62	-0.0887	5.252871	-2.57228
H63	1.320424	5.416527	-1.52525
H64	1.33943	4.281761	-2.87771
C64	2.613428	2.905984	-0.77255
H65	2.867419	3.869493	-1.20999
H66	3.16354	2.814044	0.168179
H67	2.99301	2.126548	-1.44464
C67	-2.16009	4.406167	-1.58995
H68	-2.09977	4.358615	-2.68262
H69	-3.19134	4.221428	-1.29664
H70	-1.91252	5.434372	-1.30385
C70	1.667903	0.740035	0.877298
H71	2.484953	0.52413	0.188802
H72	2.120699	1.1914	1.771968
H73	1.218847	-0.20777	1.166404

Table S421. $[\text{Rh}^{\text{IV}}(\text{bisq}^{\text{Me4}})(\text{Me}_{\text{ax}})(\text{TFA})_2]^+$
thermodynamic values

Temp	298.15	498.15
E _{gas}	-2391.86	-2391.86
E _{solv}	-2391.94	-2391.94
G	-2391.45	-2391.53
ZPE	339.896	339.896
H _{vib}	24.720	64.193
S _{trans}	45.652	48.202
S _{rot}	37.901	39.431
S _{vib}	159.319	258.915
solv	-47.6	-47.6

Table S422. $[\text{Rh}^{\text{IV}}(\text{bisq}^{\text{Me4}})(\text{Me}_{\text{eq}})(\text{TFA})_2]^+$
Cartesian coordinates

Atom	x	y	z
Rh1	-1.52636	0.338302	-1.87272

N2	-2.07345	-1.12035	-0.11569
C3	-2.59795	-2.29556	-0.43911
C4	-3.1452	-3.18324	0.509337
C5	-3.17332	-2.80665	1.830422
C6	-6.23986	1.393532	-1.36408
C7	-5.8327	0.520375	-2.34716
C8	-4.45928	0.263436	-2.51012
N9	-3.53717	0.84826	-1.75133
H10	-2.59509	-2.54674	-1.49395
H11	-3.54253	-4.13624	0.178059
H12	-3.60606	-3.45412	2.58841
O13	-2.04945	-1.20246	-3.09469
H14	-4.09191	-0.44285	-3.24661
O15	0.400969	-0.01313	-1.89223
C16	1.363363	-0.0114	-2.80113
O17	1.616515	0.916608	-3.53615
C18	2.313683	-1.22051	-2.6459
F19	3.004471	-1.43951	-3.75683
F20	3.18935	-0.92853	-1.64439
F21	1.65743	-2.33429	-2.29606
C22	-1.30363	-1.73517	-4.03038
O23	-0.17601	-1.45881	-4.37486
C24	-2.1077	-2.86944	-4.72688
F25	-1.40756	-3.43843	-5.69928
F26	-2.44609	-3.81515	-3.8223
F27	-3.25031	-2.36894	-5.24538
C28	-3.8982	1.755343	-0.7779
C29	-5.2789	2.03886	-0.54656
C30	-5.63123	2.955895	0.475256
C31	-4.64985	3.569569	1.219327
C32	-3.28767	3.301978	0.960449
C33	-2.89111	2.411168	-0.02361
H34	-6.68135	3.166655	0.653989
H35	-4.91574	4.273257	2.001667
H36	-2.52729	3.81691	1.540799
C37	-2.04262	-0.73368	1.202097
C38	-2.61797	-1.56165	2.218137
C39	-2.58879	-1.13802	3.570074
C40	-1.98737	0.051572	3.908156
C41	-1.37987	0.843016	2.910653

C42	-1.39495	0.478522	1.573372
H43	-3.03087	-1.77593	4.329992
H44	-1.9563	0.378203	4.942767
H45	-0.87125	1.758585	3.199188
H46	-6.54347	0.016907	-2.99256
H47	-7.29446	1.60202	-1.2069
C48	-1.41902	2.199629	-0.29787
C49	-0.67455	1.344053	0.588206
C50	0.72725	1.394066	0.60742
C51	1.399563	2.351331	-0.18859
C52	0.684665	3.256736	-1.01065
C53	-0.71706	3.206835	-1.0501
C58	-1.51789	1.520651	-3.59819
H59	-1.86697	0.879262	-4.40383
H60	-2.17626	2.370877	-3.44862
H61	-0.4706	1.796259	-3.72304
C61	2.907958	2.366372	-0.16255
H62	3.334293	3.244256	-0.64252
H63	3.288859	2.322375	0.862095
H64	3.30054	1.482265	-0.68082
C64	1.450526	4.263564	-1.84363
H65	0.798993	4.920356	-2.41628
H66	2.084493	4.901396	-1.21888
H67	2.103065	3.747342	-2.55626
C67	-1.49099	4.259239	-1.81274
H68	-1.17387	4.322615	-2.85703
H69	-2.5651	4.079258	-1.797
H70	-1.32016	5.247622	-1.36937
C70	1.542787	0.397437	1.400885
H71	2.227349	-0.13688	0.733502
H72	2.155855	0.885955	2.166882
H73	0.91854	-0.34293	1.898483

Table S423. $[\text{Rh}^{\text{IV}}(\text{bisq}^{\text{Me4}})(\text{Me}_{\text{eq}})(\text{TFA})_2]^+$
thermodynamic values

Temp	298.15	498.15
E_{gas}	-2391.85	-2391.85
E_{solv}	-2391.92	-2391.92
G	-2391.43	-2391.51

ZPE	340.273	340.273
H_{vib}	24.905	64.325
S_{trans}	45.652	48.202
S_{rot}	37.986	39.516
S_{vib}	161.254	260.719
solv	-42.2	-42.2

Table S424. $[\text{Rh}^{\text{I-III}}(\text{bisq}^{\text{Me4}})(\text{Me}_{\text{ax}}\cdots\text{H}_{\text{eq}})(\text{TFA}_{\text{eq}})]^{\ddagger}$
Cartesian coordinates

Atom	x	y	z
Rh1	-1.59035	-0.07624	-1.84794
N2	-1.68386	-1.23277	0.113477
C3	-1.89557	-2.52414	-0.09672
C4	-2.4339	-3.39189	0.878884
C5	-2.76823	-2.87522	2.107155
C6	-6.28832	1.076642	-1.0694
C7	-5.8846	0.033066	-1.86265
C8	-4.5061	-0.17601	-2.05074
N9	-3.55453	0.574918	-1.49902
H10	-1.63698	-2.89283	-1.08474
H11	-2.58582	-4.4393	0.63987
H12	-3.20957	-3.50119	2.878805
H13	-4.1582	-0.98998	-2.67537
O14	0.290336	-0.87195	-2.08192
C15	1.235658	-0.27683	-2.71504
O16	1.226	0.739216	-3.40232
C17	2.576888	-1.04042	-2.53339
F18	3.615874	-0.35627	-3.04273
F19	2.851661	-1.26172	-1.22251
F20	2.541507	-2.24649	-3.14177
H21	-1.39713	0.910951	-3.03772
C22	-3.92468	1.641045	-0.69604
C23	-5.31697	1.912988	-0.4679
C24	-5.70844	3.006372	0.343874
C25	-4.75857	3.817894	0.911991
C26	-3.39204	3.553712	0.687359
C27	-2.94641	2.494119	-0.0894
H28	-6.76872	3.186023	0.499781
H29	-5.04982	4.660509	1.532323

H30	-2.64607	4.202992	1.136575
C31	-1.92712	-0.7072	1.356667
C32	-2.51423	-1.50901	2.388016
C33	-2.79978	-0.93136	3.650945
C34	-2.48251	0.383783	3.891907
C35	-1.84542	1.154823	2.893105
C36	-1.55258	0.644493	1.640557
H37	-3.25668	-1.54849	4.420356
H38	-2.69471	0.83071	4.858973
H39	-1.54981	2.175179	3.11908
H40	-6.5942	-0.62997	-2.34595
H41	-7.34151	1.279544	-0.89433
C42	-1.4581	2.333435	-0.22667
C43	-0.77697	1.468655	0.65629
C44	0.629669	1.391673	0.635148
C45	1.347831	2.20125	-0.26605
C46	0.668868	3.090031	-1.12342
C47	-0.73588	3.161522	-1.11124
C50	-1.90907	-0.18186	-3.96799
H51	-2.80103	0.33588	-4.33125
H52	-1.05986	0.033843	-4.61802
H53	-2.07887	-1.2651	-3.9704
C54	1.466071	3.898167	-2.12294
H55	0.905238	4.744507	-2.52179
H56	2.389733	4.290277	-1.68771
H57	1.745422	3.250842	-2.96417
C58	2.85552	2.093726	-0.37804
H59	3.351474	3.029405	-0.08917
H60	3.266393	1.298647	0.241989
H61	3.147381	1.880801	-1.41189
C61	-1.45753	4.0594	-2.09613
H62	-2.5405	3.960131	-2.01836
H63	-1.21348	5.117669	-1.94242
H64	-1.1755	3.809712	-3.12512
C64	1.366351	0.414352	1.52972
H65	1.836871	-0.36963	0.926632
H66	2.157402	0.907813	2.104379
H67	0.700047	-0.07069	2.243223

Table S425. $[\text{Rh}^{\text{I-III}}(\text{bisq}^{\text{Me4}})(\text{Me}_{\text{ax}}\cdots\text{H}_{\text{eq}})(\text{TFA}_{\text{eq}})]^{\ddagger}$
thermodynamic values

Temp	298.15	498.15
E _{gas}	-1866.53	-1866.53
E _{solv}	-1866.55	-1866.55
G	-1866.08	-1866.15
ZPE	325.089	325.089
H _{vib}	21.010	55.105
S _{trans}	45.157	47.707
S _{rot}	37.168	38.698
S _{vib}	135.093	221.035
solv	-13.2	-13.2

Table S426. $[\text{Rh}^{\text{I-III}}(\text{bisq}^{\text{Me4}})(\text{Me}_{\text{eq}}\cdots\text{H}_{\text{ax}})(\text{TFA}_{\text{eq}})]^{\ddagger}$
Cartesian coordinates

Atom	x	y	z
Rh1	-1.39678	0.301111	-1.75854
N2	-1.72361	-1.08419	-0.03917
C3	-1.99175	-2.33952	-0.38056
C4	-2.57563	-3.26872	0.509041
C5	-2.89248	-2.86525	1.783205
C6	-6.15802	1.332314	-1.24091
C7	-5.674	0.419199	-2.14321
C8	-4.28194	0.247563	-2.25089
N9	-3.38831	0.924656	-1.52964
H10	-1.71192	-2.61739	-1.39228
H11	-2.77203	-4.27935	0.166537
H12	-3.36376	-3.54494	2.489034
H13	-1.60746	0.056396	-3.28801
H14	-3.87021	-0.48035	-2.93961
O15	0.564857	-0.30408	-1.96794
C16	0.861297	-1.48957	-2.35897
O17	0.142708	-2.43932	-2.65699
C18	2.402837	-1.6647	-2.44856
F19	2.755148	-2.92669	-2.73096
F20	2.928932	-0.86592	-3.40211
F21	3.006601	-1.33297	-1.274
C22	-3.84046	1.874812	-0.62838

C23	-5.25076	2.088825	-0.46043
C24	-5.72139	3.050938	0.467914
C25	-4.83198	3.793912	1.203317
C26	-3.44711	3.597617	1.026797
C27	-2.92704	2.666967	0.140376
H28	-6.7939	3.187322	0.577501
H29	-5.18514	4.534439	1.914956
H30	-2.74939	4.199999	1.601346
C31	-1.95813	-0.67331	1.249519
C32	-2.57999	-1.54655	2.198416
C33	-2.84295	-1.08348	3.51253
C34	-2.47479	0.18818	3.881022
C35	-1.81533	1.029916	2.957454
C36	-1.546	0.631525	1.659552
H37	-3.32513	-1.75394	4.219471
H38	-2.66885	0.54608	4.888084
H39	-1.48876	2.015374	3.277042
H40	-6.33188	-0.17717	-2.76628
H41	-7.22547	1.492646	-1.11475
C42	-1.4324	2.562856	0.039606
C43	-0.7653	1.545468	0.759478
C44	0.638948	1.455117	0.716984
C45	1.372339	2.403378	-0.02332
C46	0.712768	3.46865	-0.66721
C47	-0.69591	3.544564	-0.65399
C50	-1.12613	1.443697	-3.58293
H51	-0.515	1.037532	-4.39348
H52	-2.03316	1.895622	-3.9917
H53	-0.5292	2.201063	-3.0655
C54	1.522141	4.523279	-1.39962
H55	2.382821	4.84891	-0.80796
H56	1.912538	4.141659	-2.35171
H57	0.932558	5.412119	-1.6252
C58	2.871772	2.22073	-0.13304
H59	3.33064	2.921816	-0.82935
H60	3.370865	2.343764	0.837183
H61	3.101575	1.210717	-0.48733
C61	-1.40525	4.638358	-1.43041
H62	-2.48495	4.489272	-1.44638
H63	-1.21983	5.631717	-1.00259

H64	-1.06456	4.668624	-2.47102
C64	1.37233	0.328917	1.409766
H65	0.722174	-0.23901	2.075842
H66	1.780066	-0.36279	0.664463
H67	2.214699	0.700388	2.003573

Table S427. $[\text{Rh}^{\text{I-III}}(\text{bisq}^{\text{Me4}})(\text{Me}_{\text{eq}}\cdots\text{H}_{\text{ax}})(\text{TFA}_{\text{eq}})]^{\dagger}$
thermodynamic values

Temp	298.15	498.15
E_{gas}	-1866.54	-1866.54
E_{solv}	-1866.56	-1866.56
G	-1866.09	-1866.16
ZPE	325.225	325.225
H_{vib}	20.967	55.023
S_{trans}	45.157	47.707
S_{rot}	37.204	38.734
S_{vib}	134.994	220.836
solv	-13.6	-13.6

Table S428. $[\text{Rh}^{\text{I-III}}(\text{bisq}^{\text{Me4}})(\text{Me}_{\text{eq}}\cdots\text{H}_{\text{eq}})(\text{TFA}_{\text{ax}})]^{\dagger}$
Cartesian coordinates

Atom	x	y	z
Rh1	-1.37354	0.367085	-1.93471
N2	-2.24415	-0.98311	-0.44879
C3	-2.9392	-2.07016	-0.74881
C4	-3.46928	-2.92899	0.239765
C5	-3.26767	-2.63614	1.56795
C6	-6.48806	1.369224	-1.32891
C7	-6.13193	0.658771	-2.45052
C8	-4.75624	0.522522	-2.76352
N9	-3.79947	1.062502	-2.03708
H10	-3.06751	-2.26931	-1.80819
H11	-4.02817	-3.80706	-0.06722
H12	-3.66572	-3.27655	2.350379
O13	-1.96251	-1.01901	-3.33438
H14	-4.42551	-0.06262	-3.62003
H15	0.095694	0.431576	-2.48204
C16	-1.20995	-1.74058	-4.09719

O17	0.003132	-1.7974	-4.20147
C18	-2.10574	-2.66286	-4.97116
F19	-1.39392	-3.41303	-5.81966
F20	-2.82865	-3.50603	-4.18699
F21	-2.99231	-1.9431	-5.69764
C22	-4.12338	1.778601	-0.92303
C23	-5.48232	1.955673	-0.51575
C24	-5.76491	2.695658	0.659446
C25	-4.73422	3.238421	1.391506
C26	-3.39258	3.072498	0.976021
C27	-3.06333	2.354333	-0.1608
H28	-6.79899	2.827521	0.968341
H29	-4.94533	3.806803	2.292869
H30	-2.5979	3.526898	1.561069
C31	-2.0157	-0.67238	0.866101
C32	-2.52071	-1.48415	1.924707
C33	-2.24138	-1.11549	3.264689
C34	-1.48444	0.003947	3.526808
C35	-0.98066	0.794438	2.468943
C36	-1.23432	0.478536	1.144802
H37	-2.62477	-1.73152	4.073995
H38	-1.26685	0.286523	4.55287
H39	-0.3807	1.671147	2.697562
H40	-6.87926	0.198209	-3.08922
H41	-7.53228	1.489251	-1.05007
C42	-1.61167	2.28293	-0.58793
C43	-0.71261	1.353378	0.035067
C44	0.711791	1.599644	-0.01192
C45	1.187176	2.774906	-0.57212
C46	0.282466	3.727137	-1.14739
C47	-1.07927	3.470826	-1.20573
C50	-0.28608	1.409471	-3.52303
H51	0.058087	0.760798	-4.3283
H52	-1.17326	1.957564	-3.8537
H53	0.489435	2.128319	-3.2535
C55	0.848112	5.008631	-1.72413
H56	1.617879	5.433697	-1.07327
H57	1.320371	4.837047	-2.70092
H58	0.081609	5.771353	-1.86361
C59	2.671322	3.076008	-0.61299

H60	2.923426	3.932985	0.024953
H61	3.275198	2.23415	-0.27623
H62	3.000715	3.332209	-1.62646
C62	-2.02312	4.427261	-1.90814
H63	-2.99673	3.969206	-2.08264
H64	-2.19278	5.345462	-1.331
H65	-1.62508	4.725546	-2.88304
C65	1.652352	0.549101	0.546762
H66	1.113576	-0.3563	0.826602
H67	2.400435	0.261424	-0.19863
H68	2.193302	0.902054	1.43353

Table S429. $[\text{Rh}^{\text{I-III}}(\text{bisq}^{\text{Me4}})(\text{Me}_{\text{eq}}\cdots\text{H}_{\text{eq}})(\text{TFA}_{\text{ax}})]^{\dagger}$
thermodynamic values

Temp	298.15	498.15
E_{gas}	-1866.52	-1866.52
E_{solv}	-1866.54	-1866.54
G	-1866.07	-1866.14
ZPE	324.521	324.521
H_{vib}	21.234	55.380
S_{trans}	45.157	47.707
S_{rot}	37.308	38.838
S_{vib}	137.821	223.896
solv	-13.6	-13.6

Table S430. $[\text{Rh}^{\text{I-III}}(\text{bisq}^{\text{Me4}})(\text{H}_{\text{ax}}\cdots\text{TFA}_{\text{eq}})(\text{Me}_{\text{eq}})]^{\dagger}$
Cartesian coordinates

Atom	x	y	z
Rh1	-1.32259	0.530475	-1.8284
N2	-1.79434	-0.88384	-0.06702
C3	-2.21725	-2.08904	-0.42674
C4	-2.71154	-3.05352	0.476646
C5	-2.76329	-2.73948	1.811791
C6	-6.1122	1.210452	-1.68168
C7	-5.48937	0.655286	-2.77222
C8	-4.08226	0.616273	-2.80878
N9	-3.30386	1.099315	-1.83939
H10	-2.16435	-2.31282	-1.48709

H11	-3.04172	-4.01712	0.102647
H12	-3.14228	-3.44757	2.544068
H13	-1.23914	-0.78361	-2.95766
H14	-3.56159	0.151719	-3.63655
O15	0.681763	-0.31403	-1.96785
C16	0.605597	-1.26697	-2.76572
O17	-0.45997	-1.64326	-3.36608
C18	1.860513	-2.09999	-3.06707
F19	1.682582	-3.36533	-2.63564
F20	2.097017	-2.13799	-4.38974
F21	2.94587	-1.60305	-2.46011
C22	-3.89918	1.758571	-0.77607
C23	-5.3274	1.787718	-0.65275
C24	-5.92822	2.404205	0.474215
C25	-5.14859	3.00268	1.433375
C26	-3.7467	3.030886	1.277846
C27	-3.10524	2.4377	0.202173
H28	-7.01221	2.400966	0.554118
H29	-5.60406	3.477239	2.297819
H30	-3.1419	3.554374	2.012303
C31	-1.80993	-0.55165	1.266949
C32	-2.30447	-1.47305	2.250256
C33	-2.31399	-1.1151	3.621974
C34	-1.83242	0.110261	4.013908
C35	-1.33002	1.010472	3.049402
C36	-1.3096	0.718151	1.694811
H37	-2.69777	-1.82733	4.347809
H38	-1.8294	0.391727	5.063097
H39	-0.93718	1.969873	3.374561
H40	-6.05209	0.22619	-3.59466
H41	-7.19552	1.231289	-1.59687
C42	-1.6189	2.620087	0.074035
C43	-0.7432	1.75362	0.766119
C44	0.650695	1.961086	0.716347
C45	1.154742	3.064088	0.001779
C46	0.280724	3.941049	-0.67066
C47	-1.11103	3.728748	-0.63412
C48	-0.91612	1.678755	-3.48853
H49	-0.33474	1.124848	-4.23789
H50	-1.8254	2.052447	-3.97987

H51	-0.31669	2.542403	-3.16829
C52	2.647644	3.307669	-0.0765
H53	2.890479	4.367832	0.045353
H54	3.198804	2.755804	0.685057
H55	3.046339	2.998644	-1.05218
C56	0.865588	5.103283	-1.44911
H57	1.713542	4.781553	-2.06189
H58	0.139816	5.562669	-2.11946
H59	1.238914	5.891335	-0.78054
C60	-2.04266	4.668906	-1.37305
H61	-3.08996	4.465643	-1.1491
H62	-1.85038	5.715683	-1.11378
H63	-1.91485	4.571203	-2.45797
C64	1.602332	0.976857	1.367844
H65	1.072043	0.132499	1.808271
H66	2.299507	0.573155	0.625987
H67	2.199311	1.440468	2.163042

Table S431. $[\text{Rh}^{\text{I-III}}(\text{bisq}^{\text{Me4}})(\text{H}_{\text{ax}}\cdots\text{TFA}_{\text{eq}})(\text{Me}_{\text{eq}})]^{\ddagger}$
thermodynamic values

Temp	298.15	498.15
E _{gas}	-1866.52	-1866.52
E _{solv}	-1866.54	-1866.54
G	-1866.07	-1866.14
ZPE	323.913	323.913
H _{vib}	21.024	55.114
S _{trans}	45.157	47.707
S _{rot}	37.289	38.819
S _{vib}	135.752	221.669
solv	-9.9	-9.9

Table S432. $[\text{Rh}^{\text{I-III}}(\text{bisq}^{\text{Me4}})(\text{H}_{\text{eq}}\cdots\text{TFA}_{\text{ax}})(\text{Me}_{\text{eq}})]^{\ddagger}$
Cartesian coordinates

Atom	x	y	z
Rh1	-1.66091	0.443308	-2.02142
N2	-2.57199	-0.88206	-0.50616
C3	-3.42616	-1.86484	-0.74568
C4	-3.92734	-2.70981	0.269688

C5	-3.52126	-2.51082	1.568581
C6	-6.67318	1.650483	-1.27051
C7	-6.41413	1.155099	-2.52579
C8	-5.06631	1.048162	-2.94677
N9	-4.03796	1.399309	-2.2002
H10	-3.72133	-1.99578	-1.78281
H11	-4.6243	-3.50007	0.009911
H12	-3.88832	-3.14243	2.373541
O13	-1.82215	-1.27975	-3.45366
H14	-4.8302	0.655356	-3.93445
H15	-0.13876	-0.54831	-2.1691
C16	-0.72001	-1.85056	-3.43731
O17	0.288402	-1.50063	-2.72556
C18	-0.48083	-3.07772	-4.33211
F19	0.001858	-4.10234	-3.60742
F20	-1.61358	-3.48017	-4.92275
F21	0.413117	-2.77776	-5.29053
C22	-4.26995	1.902282	-0.9482
C23	-5.59718	2.046563	-0.43408
C24	-5.79089	2.572566	0.868655
C25	-4.70261	2.948644	1.620655
C26	-3.39208	2.816585	1.103813
C27	-3.1479	2.294606	-0.15466
H28	-6.80206	2.675552	1.2542
H29	-4.84212	3.356789	2.617841
H30	-2.55053	3.134144	1.712524
C31	-2.14755	-0.66548	0.778408
C32	-2.60498	-1.46878	1.864493
C33	-2.11734	-1.20102	3.168345
C34	-1.21485	-0.18038	3.365565
C35	-0.76975	0.608996	2.280708
C36	-1.21867	0.388176	0.988822
H37	-2.45946	-1.81322	3.998597
H38	-0.83702	0.026583	4.362957
H39	-0.06058	1.411847	2.461888
H40	-7.21463	0.84834	-3.19189
H41	-7.69276	1.748318	-0.9054
C42	-1.72818	2.227731	-0.68403
C43	-0.77838	1.273638	-0.14837
C44	0.642112	1.55217	-0.25749

C45	1.071038	2.763444	-0.76524
C46	0.125867	3.746217	-1.22453
C47	-1.22806	3.471741	-1.24237
C48	-0.75872	1.521353	-3.5442
H49	-0.63435	0.853547	-4.40774
H50	-1.41202	2.347595	-3.84954
H51	0.218035	1.931073	-3.26936
C52	0.655858	5.079092	-1.71696
H53	1.472714	5.440735	-1.08541
H54	1.05471	5.005885	-2.73804
H55	-0.11256	5.853053	-1.72157
C56	2.548127	3.082537	-0.87518
H57	2.842436	3.877634	-0.17722
H58	3.174309	2.217574	-0.65999
H59	2.809211	3.435328	-1.87933
C61	-2.22201	4.456574	-1.82518
H62	-3.11745	3.943893	-2.17913
H63	-2.54295	5.210881	-1.09339
H64	-1.80006	4.988434	-2.68157
C65	1.62963	0.478995	0.16739
H66	1.119225	-0.44054	0.456094
H67	2.307143	0.225076	-0.65509
H68	2.253552	0.790074	1.014495

Table S433. $[\text{Rh}^{\text{I-III}}(\text{bisq}^{\text{Me4}})(\text{H}_{\text{eq}}\cdots\text{TFA}_{\text{ax}})(\text{Me}_{\text{eq}})]^{\ddagger}$
thermodynamic values

Temp	298.15	498.15
E_{gas}	-1866.51	-1866.51
E_{solv}	-1866.52	-1866.52
G	-1866.06	-1866.12
ZPE	323.349	323.349
H_{vib}	21.075	55.263
S_{trans}	45.157	47.707
S_{rot}	37.296	38.826
S_{vib}	136.256	222.429
solv	-9.4	-9.4

Table S434. $[\text{Rh}^{\text{I-III}}(\text{bisq}^{\text{Me4}})(\text{H}_{\text{eq}}\cdots\text{TFA}_{\text{eq}})(\text{Me}_{\text{ax}})]^{\ddagger}$
Cartesian coordinates

Atom	x	y	z
Rh1	-1.49698	0.295315	-1.98343
N2	-1.95274	-1.35629	0.496113
C3	-2.50185	-2.53255	0.275
C4	-3.14656	-3.30262	1.274753
C5	-3.20133	-2.80383	2.553679
C6	-6.21851	1.402688	-1.59988
C7	-5.74225	0.786521	-2.7315
C8	-4.36111	0.544633	-2.85825
N9	-3.46265	0.883924	-1.93239
H10	-2.43896	-2.90385	-0.74658
H11	-3.58001	-4.26583	1.022248
H12	-3.68282	-3.36069	3.354009
H13	-3.97244	0.039747	-3.73227
O14	0.581466	-0.34404	-2.13564
C15	1.038294	0.066483	-3.21102
O16	0.396872	0.789915	-4.06231
C17	2.493447	-0.24872	-3.58702
F18	2.615682	-0.50743	-4.89587
F19	3.273911	0.820556	-3.29685
F20	2.957095	-1.29706	-2.89892
H21	-0.63323	0.864447	-3.558
C22	-3.90746	1.561608	-0.80719
C23	-5.30085	1.817158	-0.60319
C24	-5.72487	2.489043	0.57103
C25	-4.80012	2.92518	1.489104
C26	-3.42482	2.712102	1.260415
C27	-2.95702	2.037587	0.143775
H28	-6.78768	2.660665	0.721041
H29	-5.11937	3.448919	2.385736
H30	-2.70594	3.095014	1.976451
C31	-1.99428	-0.84165	1.757913
C32	-2.61371	-1.54474	2.841601
C33	-2.60696	-0.98202	4.14321
C34	-1.99236	0.228338	4.365233
C35	-1.37609	0.920183	3.296602
C36	-1.37371	0.423977	2.003334

H37	-3.0836	-1.52518	4.955995
H38	-1.97499	0.659123	5.362385
H39	-0.88708	1.870513	3.493459
H40	-6.40661	0.471814	-3.5298
H41	-7.2795	1.591774	-1.45932
C42	-1.47638	1.891219	-0.06484
C43	-0.69648	1.189211	0.905967
C44	0.699753	1.246558	0.869506
C45	1.344474	2.071651	-0.08759
C46	0.597406	2.765269	-1.04324
C47	-0.82458	2.684304	-1.05095
C50	-1.955	-1.30918	-3.19554
H51	-2.11582	-1.03333	-4.24758
H52	-1.13167	-2.03372	-3.15552
H53	-2.86512	-1.80241	-2.82876
C54	1.310285	3.624714	-2.06904
H55	0.676013	3.855268	-2.92441
H56	1.637996	4.580726	-1.63735
H57	2.201435	3.12351	-2.45562
C58	2.854598	2.199089	-0.07697
H59	3.171874	3.218024	-0.31545
H60	3.27968	1.945592	0.895188
H61	3.316788	1.53773	-0.82088
C61	-1.60107	3.65486	-1.926
H62	-2.67461	3.589322	-1.75846
H63	-1.29735	4.686821	-1.70882
H64	-1.42639	3.474958	-2.99002
C64	1.537763	0.395866	1.803974
H65	2.32346	-0.12625	1.248527
H66	2.032742	0.99255	2.580829
H67	0.935917	-0.35976	2.308211

Table S435. $[\text{Rh}^{\text{I-III}}(\text{bisq}^{\text{Me4}})(\text{H}_{\text{eq}}\cdots\text{TFA}_{\text{eq}})(\text{Me}_{\text{ax}})]^{\ddagger}$
thermodynamic values

Temp	298.15	498.15
E _{gas}	-1866.51	-1866.51
E _{solv}	-1866.52	-1866.52
G	-1866.05	-1866.12
ZPE	324.245	324.245

H_{vib}	20.852	54.928
S_{trans}	45.157	47.707
S_{rot}	37.289	38.819
S_{vib}	133.947	219.829
solv	-8.4	-8.4

Table S436.

[Rh^{III}(bisq^{Me4})(Me_{ax}...H...TFA_{eq})(TFA_{eq})]⁺

Cartesian coordinates

Atom	x	y	z
Rh1	-2.6568	0.354972	-1.44125
N2	-1.33149	-0.75596	-0.12064
C3	-1.3623	-2.08387	-0.20955
C4	-0.70127	-2.95243	0.674808
C5	0.014843	-2.41429	1.714075
C6	-5.92814	-0.42235	2.135767
C7	-6.02079	-1.16054	0.980811
C8	-5.11832	-0.90524	-0.0693
N9	-4.18567	0.03817	-0.01587
H10	-1.94266	-2.50246	-1.01594
H11	-0.78169	-4.02266	0.522021
H12	0.524437	-3.04663	2.435603
H13	-5.16581	-1.50009	-0.97008
O14	-1.07292	0.891882	-2.67061
C15	-0.57032	-0.01067	-3.394
O16	-0.94125	-1.20588	-3.44296
C17	0.651291	0.413365	-4.23956
F18	0.840238	-0.40722	-5.26671
F19	0.501769	1.665685	-4.69651
F20	1.746652	0.383487	-3.44901
O21	-4.00525	1.352945	-2.62327
C22	-3.92028	1.306002	-3.92394
O23	-3.09528	0.757586	-4.63003
C24	-5.145	2.003141	-4.58199
F25	-4.96372	2.163469	-5.89024
F26	-6.24394	1.246985	-4.38593
F27	-5.38759	3.222743	-4.04111
H28	-2.15586	-1.18233	-2.88564
C29	-3.44225	-1.49398	-2.69173

H30	-3.28547	-1.84058	-3.72216
H31	-3.53814	-2.36032	-2.03828
H32	-4.36917	-0.9324	-2.74348
C33	0.108234	-1.00857	1.837901
C34	-0.56325	-0.18069	0.877039
C35	-0.38904	1.230471	0.948546
C36	0.382441	1.758976	1.972653
C37	1.003615	0.949145	2.944425
C38	0.875137	-0.41638	2.872583
H39	0.519115	2.835607	2.015065
H40	1.593882	1.408842	3.730662
H41	1.367848	-1.06403	3.591733
C42	-4.1101	0.843089	1.104797
C43	-4.96177	0.60806	2.229105
C44	-4.82645	1.420365	3.382948
C45	-3.90032	2.436909	3.40792
C46	-3.10195	2.693463	2.27248
C47	-3.1948	1.925035	1.12403
H48	-5.47111	1.23112	4.236081
H49	-3.79531	3.062961	4.288377
H50	-2.41173	3.532253	2.288158
H51	-6.592	-0.60772	2.975431
H52	-6.76025	-1.94395	0.859807
C53	-0.97285	2.161311	-0.05671
C54	-2.40447	2.322111	-0.09787
C55	-2.96154	3.351421	-0.94111
C56	-2.12425	4.06165	-1.81288
C57	-0.72441	3.865031	-1.76443
C58	-0.14222	2.90634	-0.89418
C61	-2.72186	5.062011	-2.78166
H62	-2.15514	5.101594	-3.71374
H63	-3.74608	4.801699	-3.04535
H64	-2.73298	6.076849	-2.36254
C65	0.185105	4.661421	-2.66508
H66	-0.25245	5.611956	-2.96761
H67	1.145218	4.869917	-2.18976
H68	0.397025	4.084565	-3.57573
C68	1.3519	2.663774	-0.95928
H69	1.647983	1.781551	-0.39353
H70	1.671845	2.510864	-1.99331

H71	1.92283	3.513563	-0.56668
C71	-4.4209	3.71459	-0.85
H72	-4.92764	3.205196	-0.03218
H73	-4.53255	4.793471	-0.69546
H74	-4.93861	3.457628	-1.77632

Table S437.

[Rh^{III}(bisq^{Me4})(Me_{ax}...H...TFA_{eq})(TFA_{eq})]⁺⁺
thermodynamic values

Temp	298.15	498.15
E_{gas}	-2392.47	-2392.47
E_{solv}	-2392.53	-2392.53
G	-2392.04	-2392.12
ZPE	344.800	344.800
H_{vib}	24.718	64.243
S_{trans}	45.656	48.206
S_{rot}	37.933	39.463
S_{vib}	158.533	258.240
solv	-41.9	-41.9

Table S438.

[Rh^{III}(bisq^{Me4})(Me_{eq}...H...TFA_{ax})(TFA_{eq})]⁺⁺
Cartesian coordinates

Atom	x	y	z
Rh1	-1.41019	0.127903	-1.57095
N2	-1.90081	-1.29494	-0.07262
C3	-2.07421	-2.58374	-0.3327
C4	-2.60569	-3.47593	0.621474
C5	-2.98451	-2.99652	1.854205
C6	-6.19523	1.354479	-1.40906
C7	-5.71029	0.296689	-2.1363
C8	-4.32682	0.053175	-2.13193
N9	-3.44395	0.804144	-1.4748
H10	-1.81391	-2.9159	-1.33025
H11	-2.72421	-4.5206	0.356575
H12	-3.42701	-3.6548	2.596552
H13	-3.92395	-0.78725	-2.68159
O14	0.423622	-0.78372	-1.65663

C15	1.494966	-0.26521	-2.18143
O16	1.68771	0.85627	-2.61481
C17	2.661226	-1.29465	-2.16611
F18	3.154587	-1.39459	-0.90232
F19	2.255748	-2.51811	-2.54407
F20	3.655118	-0.9086	-2.96466
H21	-0.44139	1.868697	-4.05129
H22	-0.7545	0.513985	-3.70022
O23	-1.93799	-1.35755	-2.92972
C24	-1.35213	-1.3737	-4.05417
O25	-0.63843	-0.45904	-4.5152
C26	-1.61364	-2.63885	-4.90068
F27	-0.91095	-2.62762	-6.02586
F28	-1.29317	-3.72645	-4.18348
F29	-2.9251	-2.68855	-5.19479
C30	-1.02132	1.743453	-3.12257
H31	-2.01135	2.162301	-3.30271
H32	-0.42989	2.315722	-2.42033
C33	-5.29776	2.176608	-0.68839
C34	-3.8926	1.889144	-0.7432
C35	-2.98887	2.745841	-0.0454
C36	-3.50936	3.805029	0.68549
C37	-4.89	4.074763	0.755637
C38	-5.77179	3.27528	0.071349
H39	-2.82018	4.447716	1.224847
H40	-5.24483	4.914917	1.343899
H41	-6.83996	3.469332	0.096183
C42	-2.18458	-0.80121	1.174877
C43	-2.7791	-1.62996	2.171047
C44	-3.1069	-1.05787	3.426443
C45	-2.81909	0.264462	3.677389
C46	-2.16365	1.053069	2.703862
C47	-1.83531	0.540462	1.461211
H48	-3.57259	-1.68034	4.184772
H49	-3.06418	0.70293	4.639614
H50	-1.88373	2.073426	2.949294
H51	-7.2583	1.57557	-1.37604
H52	-6.36065	-0.35717	-2.7062
C53	-1.51047	2.554041	-0.04205
C54	-0.97498	1.340081	0.508612

C55	0.452497	1.208075	0.663834
C56	1.293867	2.23081	0.209748
C57	0.740522	3.431021	-0.29772
C58	-0.65737	3.588099	-0.45971
C61	1.670143	4.552398	-0.69232
H62	2.524924	4.616933	-0.01597
H63	2.0721	4.379496	-1.70004
H64	1.173528	5.522195	-0.6967
C65	2.79745	2.073581	0.291396
H66	3.285936	2.536006	-0.56799
H67	3.204242	2.541562	1.197723
H68	3.095632	1.02577	0.297753
C68	-1.18809	4.835354	-1.14339
H69	-2.22926	4.723201	-1.44345
H70	-1.12573	5.718826	-0.49671
H71	-0.60873	5.058757	-2.04387
C71	1.049301	0.019875	1.380388
H72	0.297636	-0.59168	1.875295
H73	1.595752	-0.62449	0.686703
H74	1.760765	0.353866	2.142383

Table S439.

$[\text{Rh}^{\text{III}}(\text{bisq}^{\text{Me4}})(\text{Me}_{\text{eq}}\cdots\text{H}\cdots\text{TFA}_{\text{ax}})(\text{TFA}_{\text{eq}})]^{+\ddagger}$
thermodynamic values

Temp	298.15	498.15
E _{gas}	-2392.47	-2392.47
E _{solv}	-2392.53	-2392.53
G	-2392.04	-2392.12
ZPE	344.951	344.951
H _{vib}	24.728	64.181
S _{trans}	45.656	48.206
S _{rot}	38.038	39.568
S _{vib}	159.409	258.932
solv	-39.9	-39.9

Table S440.

$[\text{Rh}^{\text{III}}(\text{bisq}^{\text{Me4}})(\text{Me}_{\text{eq}}\cdots\text{H}\cdots\text{TFA}_{\text{eq}})(\text{TFA}_{\text{ax}})]^{+\ddagger}$
Cartesian coordinates

Atom	x	y	z
Rh1	-2.47534	0.098009	-1.45171
N2	-1.34678	-1.14239	-0.15985
C3	-1.44048	-2.46541	-0.20994
C4	-0.80622	-3.3014	0.730442
C5	-0.08679	-2.73456	1.755495
C6	-5.66301	-0.02337	2.267423
C7	-5.72741	-0.92421	1.232734
C8	-4.82988	-0.79541	0.15676
N9	-3.92881	0.180377	0.081144
H10	-2.0543	-2.87506	-1.00246
H11	-0.91289	-4.376	0.633868
H12	0.393058	-3.35194	2.509725
H13	-4.8275	-1.50936	-0.65794
O14	-0.9857	-0.27379	-2.84953
C15	-1.0602	0.367183	-3.93723
O16	-1.86677	1.28948	-4.18972
C17	-0.0091	0.013566	-5.01232
F18	1.034985	0.869404	-4.87711
F19	0.446857	-1.23	-4.85712
F20	-0.51273	0.153402	-6.23492
H21	-4.04858	2.058843	-3.45599
H22	-2.78614	1.233505	-3.24339
O23	-3.38501	-1.59015	-2.11335
C24	-3.50428	-1.95877	-3.36693
O25	-3.19356	-1.38	-4.38336
C26	-4.15966	-3.36887	-3.403
F27	-4.35585	-3.78406	-4.64791
F28	-3.36118	-4.25879	-2.76864
F29	-5.34599	-3.35018	-2.7574
C30	-4.02995	1.269439	-2.68999
H31	-4.6695	0.464938	-3.04484
H32	-4.43998	1.739666	-1.80201
C33	-3.86821	1.136871	1.074464
C34	-4.72777	1.038679	2.215164
C35	-4.63751	2.008866	3.244176
C36	-3.7468	3.050471	3.136885
C37	-2.93405	3.165206	1.989891
C38	-2.97648	2.237122	0.960977
H39	-5.2901	1.917895	4.107406

H40	-3.67456	3.796743	3.921558
H41	-2.25842	4.011201	1.902274
C42	-0.58536	-0.54012	0.813171
C43	0.044955	-1.32541	1.826407
C44	0.790575	-0.67243	2.839649
C45	0.919816	0.697025	2.827789
C46	0.336051	1.457282	1.790274
C47	-0.40648	0.865657	0.782205
H48	1.263787	-1.27118	3.61228
H49	1.492918	1.199843	3.600259
H50	0.494644	2.531782	1.767365
H51	-6.43977	-1.74143	1.227559
H52	-6.32468	-0.10532	3.125121
C53	-0.89272	1.712693	-0.36801
C54	-2.10555	2.456901	-0.23879
C55	-2.35954	3.561376	-1.09181
C56	-1.39141	3.93768	-2.03408
C57	-0.16932	3.216596	-2.15953
C58	0.079115	2.104798	-1.34812
C61	-1.68014	5.126633	-2.92196
H62	-0.83556	5.407858	-3.54673
H63	-2.52262	4.912302	-3.5914
H64	-1.96578	6.003039	-2.33019
C65	0.85885	3.674764	-3.17327
H66	1.101646	4.733578	-3.03844
H67	1.791343	3.118638	-3.10247
H68	0.482358	3.552227	-4.19512
C68	-3.64815	4.349827	-0.98951
H69	-4.37734	3.869239	-0.33765
H70	-3.47111	5.357855	-0.59465
H71	-4.11127	4.477475	-1.97291
C71	1.381465	1.340224	-1.45966
H72	1.354651	0.408391	-0.89794
H73	1.603523	1.088141	-2.49807
H74	2.222642	1.932053	-1.0789

Table S441.

$[\text{Rh}^{\text{III}}(\text{bisq}^{\text{Me4}})(\text{Me}_{\text{eq}}\cdots\text{H}\cdots\text{TFA}_{\text{eq}})(\text{TFA}_{\text{ax}})]^{+\ddagger}$
thermodynamic values

Temp	298.15	498.15
E _{gas}	-2392.48	-2392.48
E _{solv}	-2392.54	-2392.54
G	-2392.05	-2392.13
ZPE	344.797	344.797
H _{vib}	24.789	64.266
S _{trans}	45.656	48.206
S _{rot}	38.008	39.538
S _{vib}	160.841	260.429
solv	-40.2	-40.2

Table S442. $[\text{Rh}^{\text{III}}(\text{bisq}^{\text{Me4}})(\text{Me}_{\text{ax}}\cdots\text{TFA}_{\text{eq}})(\text{TFA}_{\text{eq}})]^{\ddagger}$
Cartesian coordinates

Atom	x	y	z
Rh1	-1.59771	0.225507	-1.78374
N2	-2.05271	-0.99754	-0.12616
C3	-2.5205	-2.20842	-0.40896
C4	-2.94865	-3.1346	0.559581
C5	-2.88452	-2.77537	1.881944
C6	-6.36824	1.210026	-1.46918
C7	-5.84592	0.574631	-2.56889
C8	-4.44752	0.448515	-2.68239
N9	-3.58977	0.92741	-1.7845
H10	-2.5591	-2.47172	-1.4601
H11	-3.31843	-4.10409	0.243507
H12	-3.2107	-3.45236	2.666882
H13	-4.00825	-0.06191	-3.53001
O14	0.32899	-0.58278	-1.66075
C15	1.121141	-0.77471	-2.65483
O16	0.94949	-0.61891	-3.85891
C17	2.499293	-1.31762	-2.17789
F18	3.248953	-1.75391	-3.19923
F19	3.212787	-0.34548	-1.54366
F20	2.362906	-2.33871	-1.30442
O21	-1.12103	1.446425	-3.39516
C22	-1.48229	1.069315	-4.52724
O23	-2.05537	-0.00339	-4.87707
C24	-1.2782	2.118806	-5.64351
F25	-1.338	1.588226	-6.86907

F26	-2.25766	3.051162	-5.54069
F27	-0.10137	2.750294	-5.51048
C28	-4.08016	1.679582	-0.73437
C29	-5.49244	1.79453	-0.52204
C30	-5.97837	2.508323	0.602235
C31	-5.09979	3.125368	1.458968
C32	-3.71254	3.077121	1.200772
C33	-3.18247	2.381608	0.126478
H34	-7.05189	2.568528	0.75926
H35	-5.4666	3.676678	2.319773
H36	-3.03165	3.621718	1.848136
C37	-1.93675	-0.61387	1.19831
C38	-2.37122	-1.50506	2.238203
C39	-2.27149	-1.12081	3.599002
C40	-1.74306	0.100865	3.934026
C41	-1.29233	0.966917	2.916102
C42	-1.36802	0.650594	1.567123
H43	-2.6125	-1.81529	4.361916
H44	-1.65917	0.401521	4.974053
H45	-0.85232	1.920505	3.191174
H46	-6.48018	0.148466	-3.33886
H47	-7.44176	1.294026	-1.32231
C48	-1.70717	2.471021	-0.13977
C49	-0.81635	1.644163	0.5872
C50	0.571816	1.817382	0.457254
C51	1.071258	2.805997	-0.42275
C52	0.185522	3.599844	-1.17479
C53	-1.21082	3.456854	-1.01187
C58	-1.84402	-1.66349	-3.86589
H59	-1.51191	-1.99509	-4.84057
H60	-1.13015	-1.83646	-3.07603
H61	-2.88573	-1.86117	-3.64515
C61	0.66792	4.582163	-2.22251
H62	1.751669	4.606182	-2.32011
H63	0.263976	4.307825	-3.2036
H64	0.333692	5.605134	-2.01007
C64	2.57559	2.938162	-0.55605
H65	2.881526	3.892621	-0.98339
H66	3.068541	2.85011	0.416313
H67	2.982634	2.141208	-1.18976

C67	-2.14853	4.313698	-1.83493
H68	-3.18231	4.237814	-1.49456
H69	-1.86797	5.371687	-1.79986
H70	-2.12206	4.007608	-2.88799
C70	1.545205	0.917645	1.188887
H71	1.038105	0.112073	1.718839
H72	2.243212	0.458301	0.485589
H73	2.139404	1.474955	1.924937

Table S443. $[\text{Rh}^{\text{III-I}}(\text{bisq}^{\text{Me4}})(\text{Me}_{\text{ax}}\cdots\text{TFA}_{\text{eq}})(\text{TFA}_{\text{eq}})]^{\ddagger}$
thermodynamic values

Temp	298.15	498.15
E_{gas}	-2392.05	-2392.05
E_{solv}	-2392.08	-2392.08
G	-2391.59	-2391.67
ZPE	338.801	338.801
H_{vib}	25.021	64.252
S_{trans}	45.652	48.202
S_{rot}	38.003	39.533
S_{vib}	162.845	261.835
Solv	-15.8	-15.8

Table S444. $[\text{Rh}^{\text{III-I}}(\text{bisq}^{\text{Me4}})(\text{Me}_{\text{eq}}\cdots\text{TFA}_{\text{ax}})(\text{TFA}_{\text{eq}})]^{\ddagger}$
Cartesian coordinates

Atom	x	y	z
Rh1	-1.37444	0.302953	-2.10203
N2	-1.64045	-1.03611	-0.23177
C3	-1.80997	-2.31117	-0.5561
C4	-2.2443	-3.29875	0.353766
C5	-2.53538	-2.92428	1.640709
C6	-6.19913	1.30742	-1.55971
C7	-5.66248	0.493423	-2.52051
C8	-4.26357	0.373699	-2.5894
N9	-3.40791	1.013885	-1.79484
H10	-1.62744	-2.56725	-1.59369
H11	-2.3603	-4.32225	0.013301
H12	-2.90483	-3.64303	2.367942
O13	-1.98448	-1.48266	-3.45976

H14	-3.82663	-0.31003	-3.30181
O15	0.539708	-0.43263	-2.09469
C16	1.23629	-0.82512	-3.10593
O17	1.008274	-0.77641	-4.30531
C18	2.56063	-1.47912	-2.61644
F19	3.411316	-1.70246	-3.62539
F20	3.204485	-0.69957	-1.70802
F21	2.310045	-2.66323	-2.01456
C22	-1.93178	-1.02118	-4.62655
O23	-1.7476	0.158999	-5.02187
C24	-2.2903	-2.03111	-5.74217
F25	-1.85496	-1.65386	-6.94763
F26	-1.80226	-3.25094	-5.47866
F27	-3.64372	-2.12735	-5.79665
C28	-3.91305	1.876683	-0.82603
C29	-5.34036	2.016436	-0.68655
C30	-5.89771	2.860813	0.306476
C31	-5.08262	3.574199	1.147421
C32	-3.6865	3.466526	0.998183
C33	-3.07962	2.656083	0.048858
H34	-6.97979	2.929342	0.377693
H35	-5.49944	4.223897	1.910878
H36	-3.03996	4.052845	1.644408
C37	-1.83978	-0.64579	1.071005
C38	-2.33717	-1.57923	2.04094
C39	-2.59413	-1.15887	3.369693
C40	-2.33729	0.137321	3.743127
C41	-1.78855	1.039496	2.807187
C42	-1.52399	0.684939	1.494247
H43	-2.98046	-1.88244	4.083119
H44	-2.52676	0.466876	4.760532
H45	-1.53441	2.045385	3.128755
H46	-6.27636	-0.0692	-3.21516
H47	-7.27421	1.423849	-1.45064
C48	-1.58279	2.704487	-0.00959
C49	-0.8312	1.699984	0.631559
C50	0.571414	1.701847	0.544359
C51	1.21869	2.731474	-0.17152
C52	0.472724	3.783176	-0.73435
C53	-0.93926	3.763705	-0.67366

C58	-1.09903	1.433534	-3.67147
H59	-0.15108	1.456691	-4.20079
H60	-1.81822	2.178004	-4.01057
H61	-0.77217	1.86012	-2.37928
C61	1.182204	4.927138	-1.43548
H62	0.542325	5.80382	-1.54016
H63	2.073273	5.243453	-0.88657
H64	1.510227	4.643314	-2.44423
C64	2.72231	2.653083	-0.34071
H65	3.104918	3.395247	-1.04089
H66	3.249189	2.795202	0.61201
H67	3.009793	1.667884	-0.72091
C67	-1.73682	4.840703	-1.38572
H68	-2.80441	4.620943	-1.39269
H69	-1.61156	5.822892	-0.91278
H70	-1.41607	4.948351	-2.42794
C70	1.40042	0.593526	1.15392
H71	1.806598	-0.04584	0.362285
H72	2.247926	0.990724	1.723111
H73	0.815858	-0.03663	1.824752

Table S445. $[\text{Rh}^{\text{III-I}}(\text{bisq}^{\text{Me4}})(\text{Me}_{\text{eq}}\cdots\text{TFA}_{\text{ax}})(\text{TFA}_{\text{eq}})]^{\dagger}$
thermodynamic values

Temp	298.15	498.15
E _{gas}	-2392.05	-2392.05
E _{solv}	-2392.07	-2392.07
G	-2391.59	-2391.67
ZPE	336.745	336.745
H _{vib}	24.340	63.098
S _{trans}	45.652	48.202
S _{rot}	38.187	39.718
S _{vib}	162.620	261.392
solv	-16.1	-16.1

Table S446. $[\text{Rh}^{\text{III-I}}(\text{bisq}^{\text{Me4}})(\text{Me}_{\text{eq}}\cdots\text{TFA}_{\text{eq}})(\text{TFA}_{\text{ax}})]^{\dagger}$
Cartesian coordinates

Atom	x	y	z
Rh1	-1.37157	0.678651	-2.08526

N2	-1.99831	-1.10916	-0.05706
C3	-2.56988	-2.23099	-0.44929
C4	-3.15726	-3.16011	0.443953
C5	-3.14058	-2.8828	1.788743
C6	-6.16258	1.385431	-1.6236
C7	-5.67014	0.750632	-2.73929
C8	-4.27626	0.605073	-2.90053
N9	-3.4018	1.072972	-2.0166
H10	-2.56764	-2.41521	-1.52066
H11	-3.60546	-4.06986	0.05673
H12	-3.58088	-3.56745	2.509929
O13	-1.92248	-0.93985	-3.32252
H14	-3.85491	0.059424	-3.73689
O15	0.60047	0.056341	-2.04477
C16	1.37835	0.530063	-2.89944
O17	1.163414	1.390226	-3.79388
C18	2.838079	0.017811	-2.84505
F19	3.097699	-0.78701	-3.88173
F20	3.701224	1.060241	-2.89786
F21	3.090663	-0.65417	-1.70949
C22	-1.2438	-1.59781	-4.19495
O23	-0.12904	-1.39957	-4.65989
C24	-2.07977	-2.79814	-4.72541
F25	-1.42443	-3.51418	-5.64517
F26	-2.42935	-3.64047	-3.72151
F27	-3.23157	-2.35562	-5.29151
C28	-3.86446	1.709353	-0.88659
C29	-5.25946	1.883968	-0.65085
C30	-5.67405	2.529955	0.540946
C31	-4.73684	2.9801	1.442737
C32	-3.35685	2.807533	1.191733
C33	-2.90403	2.178324	0.045482
H34	-6.73669	2.657189	0.728835
H35	-5.05356	3.473715	2.356882
H36	-2.63398	3.173886	1.913911
C37	-1.95669	-0.8146	1.273419
C38	-2.53153	-1.68785	2.252039
C39	-2.46695	-1.34888	3.626943
C40	-1.83824	-0.19134	4.01998
C41	-1.2529	0.662079	3.05772

C42	-1.29673	0.383844	1.701693
H43	-2.91356	-2.01916	4.357333
H44	-1.78166	0.071846	5.072438
H45	-0.74581	1.564087	3.389873
H46	-6.33063	0.347808	-3.4998
H47	-7.23178	1.505496	-1.47051
C48	-1.43473	2.017952	-0.2345
C49	-0.63105	1.30146	0.726674
C50	0.749121	1.459302	0.738769
C51	1.360601	2.423792	-0.12193
C52	0.613204	3.108719	-1.07262
C53	-0.80548	2.905799	-1.16819
C54	-0.64255	1.719787	-4.56187
H55	-0.56758	0.793971	-5.11489
H56	-1.59674	1.941849	-4.10462
H57	-0.11989	2.575755	-4.96717
C58	1.306073	4.09858	-1.98799
H59	0.685101	4.386015	-2.83498
H60	1.576287	5.019499	-1.45336
H61	2.226398	3.674312	-2.39672
C62	2.847443	2.689224	0.004161
H63	3.084508	3.737916	-0.19063
H64	3.218889	2.450147	1.001752
H65	3.426355	2.091994	-0.71034
C67	-1.62299	3.936053	-1.93146
H68	-2.68954	3.721022	-1.90593
H69	-1.47777	4.931526	-1.49157
H70	-1.32774	4.005061	-2.98019
C71	1.641459	0.574777	1.585936
H72	2.438993	0.152719	0.965591
H73	2.121516	1.121317	2.407339
H74	1.087702	-0.25526	2.02312

Table S447. $[\text{Rh}^{\text{III}}\text{-I}(\text{bisq}^{\text{Me4}})(\text{Me}_{\text{eq}}\cdots\text{TFA}_{\text{eq}})(\text{TFA}_{\text{ax}})]^{\ddagger}$
thermodynamic values

Temp	298.15	498.15
E_{gas}	-2392.05	-2392.05
E_{solv}	-2392.07	-2392.07
G	-2391.58	-2391.66

ZPE	338.448	338.448
H_{vib}	25.169	64.449
S_{trans}	45.652	48.202
S_{rot}	38.062	39.592
S_{vib}	163.949	263.068
solv	-14.1	-14.1

Table S448. [Rh^{III}-(bisq^{Me4})(Me_{ax}...TFA)(TFA)₂]⁺
Cartesian coordinates

Atom	x	y	z
Rh1	-1.33839	0.199831	-1.87801
N2	-1.8423	-1.03777	-0.22164
C3	-2.18091	-2.29732	-0.48209
C4	-2.54561	-3.24522	0.49249
C5	-2.56022	-2.86456	1.807825
C6	-6.17558	0.789632	-1.93839
C7	-5.5042	0.346644	-3.04848
C8	-4.09416	0.401618	-3.06423
N9	-3.36543	0.852685	-2.04635
H10	-2.17243	-2.59156	-1.52066
H11	-2.81315	-4.24796	0.176227
H12	-2.84704	-3.55372	2.598268
H13	-3.55293	0.046384	-3.92794
O14	0.619885	-0.45535	-1.55469
C15	1.44469	-0.82571	-2.4633
O16	1.308333	-1.01246	-3.66563
C17	2.857115	-1.07304	-1.85042
F18	3.693281	-1.67913	-2.70991
F19	3.452171	0.101894	-1.48868
F20	2.809519	-1.83785	-0.73316
O21	-0.62199	1.534153	-3.29559
C22	-1.01381	1.724581	-4.49076
O23	-1.90311	1.190437	-5.15636
C24	-0.24732	2.900042	-5.16426
F25	-0.16779	2.75971	-6.49888
F26	-0.90725	4.074271	-4.92888
F27	1.010077	3.06778	-4.70173
C28	-4.01894	1.454618	-0.98584
C29	-5.44647	1.38744	-0.87825

C30	-6.09695	1.942949	0.252638
C31	-5.3684	2.601039	1.214593
C32	-3.97422	2.752527	1.056478
C33	-3.28578	2.206713	-0.01536
H34	-7.17838	1.856228	0.327169
H35	-5.86262	3.03562	2.07959
H36	-3.41605	3.336279	1.782786
C37	-1.79789	-0.63227	1.104606
C38	-2.17821	-1.54491	2.149186
C39	-2.15505	-1.1392	3.506451
C40	-1.74807	0.127063	3.842548
C41	-1.34811	1.015329	2.825825
C42	-1.35742	0.679555	1.479447
H43	-2.45602	-1.8554	4.266593
H44	-1.72281	0.445697	4.881191
H45	-1.00437	2.009917	3.095393
H46	-6.00685	-0.10187	-3.8976
H47	-7.2581	0.716376	-1.862
C48	-1.82404	2.515083	-0.16913
C49	-0.87671	1.738212	0.532534
C50	0.491194	2.054896	0.467393
C51	0.906351	3.144541	-0.32615
C52	-0.03653	3.933045	-1.00898
C53	-1.41163	3.621817	-0.9316
C58	-1.74946	-1.6436	-3.65175
H59	-1.66014	-0.87874	-4.40872
H60	-0.85212	-2.15007	-3.33586
H61	-2.68549	-1.76377	-3.13962
O62	-2.21293	-3.03834	-4.88085
C63	-3.47104	-3.09988	-5.09416
O64	-4.39734	-2.42428	-4.64083
C65	-3.86992	-4.272	-6.0401
F66	-2.86199	-4.71423	-6.8142
F67	-4.30301	-5.32887	-5.3038
F68	-4.88333	-3.92051	-6.85918
C68	2.393422	3.400997	-0.46147
H69	2.616439	4.288379	-1.053
H70	2.876266	3.52245	0.51659
H71	2.878653	2.548747	-0.951
C71	0.432107	5.08867	-1.87328

H72	-0.39465	5.709657	-2.21681
H73	1.128191	5.742263	-1.33622
H74	0.944121	4.717084	-2.76752
C74	-2.41872	4.437612	-1.71863
H75	-2.39839	5.4974	-1.43485
H76	-2.20213	4.381608	-2.79047
H77	-3.43808	4.082239	-1.56687
C77	1.532465	1.21973	1.179015
H78	2.249302	0.81135	0.463249
H79	2.097769	1.816737	1.907918
H80	1.090112	0.377847	1.710577

Table S449. $[\text{Rh}^{\text{III}}\text{I}(\text{bisq}^{\text{Me4}})(\text{Me}_{\text{ax}}\cdots\text{TFA})(\text{TFA})_2]^{-}$ thermodynamic values

Temp	298.15	498.15
E _{gas}	-2918.36	-2918.36
E _{solv}	-2918.43	-2918.43
G	-2917.93	-2918.03
ZPE	356.452	356.452
H _{vib}	28.860	72.959
S _{trans}	46.080	48.630
S _{rot}	39.167	40.697
S _{vib}	199.748	313.111
solv	-47.1	-47.1

Table S450. $[\text{Rh}^{\text{III}}\text{I}(\text{bisq}^{\text{Me4}})(\text{Me}_{\text{ax}}\cdots\text{TFAH})(\text{TFA})_2]^{\dagger}$ Cartesian coordinates

Atom	x	y	z
Rh1	-1.85357	0.12548	-1.73778
N2	-2.37161	-0.92101	0.041189
C3	-3.05453	-2.05364	-0.10642
C4	-3.42415	-2.90728	0.947707
C5	-3.06275	-2.56157	2.223577
C6	-6.50156	1.358401	-1.38626
C7	-5.99855	0.873999	-2.56903
C8	-4.60518	0.709119	-2.70548
N9	-3.73931	1.02644	-1.74438
H10	-3.32593	-2.31778	-1.11793

H11	-3.97699	-3.81419	0.72825
H12	-3.31713	-3.18779	3.074557
H13	-4.17472	0.323066	-3.62132
O14	0.090019	-0.8846	-1.71562
C15	0.99882	-1.18976	-2.4856
O16	1.000216	-1.46897	-3.74453
C17	2.433737	-1.26755	-1.90287
F18	3.199938	-2.14184	-2.56204
F19	3.017929	-0.0524	-1.98264
F20	2.394188	-1.62974	-0.61196
O21	-1.06733	1.240577	-3.29361
C22	-1.57281	1.503719	-4.43868
O23	-2.56874	1.038027	-4.99377
C24	-0.79309	2.626071	-5.17863
F25	-0.87164	2.493644	-6.50939
F26	-1.3326	3.833623	-4.8558
F27	0.511553	2.671875	-4.84345
C28	-4.20187	1.685064	-0.62069
C29	-5.60768	1.798027	-0.37829
C30	-6.06516	2.385118	0.829257
C31	-5.1646	2.900062	1.730416
C32	-3.78495	2.893052	1.42848
C33	-3.28481	2.315217	0.273647
H34	-7.13509	2.43988	1.011716
H35	-5.50983	3.355929	2.653827
H36	-3.09099	3.387386	2.101801
C37	-2.00012	-0.53109	1.320855
C38	-2.34388	-1.36294	2.443553
C39	-1.97042	-0.99331	3.759674
C40	-1.27833	0.170686	3.977478
C41	-0.94633	0.991331	2.882548
C42	-1.27762	0.682823	1.569828
H43	-2.24453	-1.64919	4.581431
H44	-0.98811	0.466204	4.981402
H45	-0.40467	1.915101	3.063017
H46	-6.64478	0.583609	-3.39035
H47	-7.57233	1.445208	-1.22079
C48	-1.83648	2.500022	-0.07307
C49	-0.85843	1.683644	0.534915
C50	0.50993	1.937844	0.3147

C51	0.887202	2.996771	-0.53518
C52	-0.08826	3.791562	-1.16562
C53	-1.45797	3.561761	-0.91844
C58	-2.49003	-1.71497	-3.38623
H59	-2.27991	-0.91847	-4.08141
H60	-1.70944	-2.25055	-2.87255
H61	-3.50652	-1.83495	-3.04404
O62	-2.69873	-2.99697	-4.71739
C63	-1.69541	-2.98563	-5.49904
O64	-0.62517	-2.36469	-5.39278
C65	-1.89601	-3.84701	-6.77443
F66	-2.52041	-5.0032	-6.48607
F67	-2.65557	-3.1724	-7.65932
F68	-0.72732	-4.139	-7.35937
H69	0.141081	-1.67567	-4.27687
C69	-2.50102	4.442996	-1.57748
H70	-2.29862	5.504349	-1.39837
H71	-2.50609	4.292123	-2.66228
H72	-3.50585	4.239546	-1.2078
C72	0.34831	4.880605	-2.12691
H73	-0.49187	5.345999	-2.63806
H74	0.905695	5.675183	-1.61484
H75	0.999314	4.469537	-2.90425
C75	2.361493	3.255702	-0.77429
H76	2.545969	4.243321	-1.19659
H77	2.937732	3.183381	0.153259
H78	2.781509	2.518727	-1.47017
C78	1.582223	1.085246	0.962106
H79	2.389854	0.870379	0.261661
H80	2.035718	1.592052	1.825173
H81	1.189373	0.130378	1.310639

Table S451. $[\text{Rh}^{\text{III}}\text{-I}(\text{bisq}^{\text{Me4}})(\text{Me}_{\text{ax}}\cdots\text{TFAH})(\text{TFA})_2]^{\ddagger}$ thermodynamic values

Temp	298.15	498.15
E _{gas}	-2918.85	-2918.85
E _{solv}	-2918.87	-2918.87
G	-2918.35	-2918.45
ZPE	364.611	364.611

H _{vib}	29.671	74.679
S _{trans}	46.083	48.634
S _{rot}	39.094	40.624
S _{vib}	196.319	309.957
solv	-17.0	-17.0

Table S452. $[\text{Rh}^{\text{III}}\text{-I}(\text{bisq}^{\text{Me4}})(\text{Me}_{\text{ax}}\cdots\text{TFA})(\text{TFA}_{\text{eq}})(\text{TFAH}_{\text{eq}})]^{\ddagger}$ Cartesian coordinates

Atom	x	y	z
Rh1	-0.92202	0.772482	-1.92822
N2	-2.01083	-0.47922	-0.5978
C3	-2.82334	-1.37038	-1.16484
C4	-3.57923	-2.31709	-0.44886
C5	-3.48398	-2.3391	0.916457
C6	-5.21655	2.951351	-2.25308
C7	-4.53043	2.592764	-3.38775
C8	-3.21293	2.111262	-3.25962
N9	-2.58176	2.020228	-2.09383
H10	-2.90887	-1.3802	-2.24374
H11	-4.20553	-3.00283	-1.00818
H12	-4.04017	-3.05675	1.513714
H13	-2.67043	1.757377	-4.1273
O14	0.613274	-0.70175	-1.67846
C15	1.847166	-0.75172	-1.62134
O16	2.715704	0.144373	-1.90231
C17	2.467657	-2.09472	-1.16981
F18	2.655298	-2.88592	-2.24035
F19	3.650684	-1.90973	-0.56544
F20	1.650834	-2.72555	-0.31306
O21	-0.08522	2.064939	-3.36387
C22	1.060474	2.556591	-3.50704
O23	2.147959	2.245596	-2.96705
C24	1.127876	3.764881	-4.47548
F25	0.112166	3.765745	-5.35085
F26	1.053471	4.913646	-3.75625
F27	2.277045	3.784841	-5.16148
H28	2.338815	1.07741	-2.33104
C29	-3.17713	2.548059	-0.96521

C30	-4.54938	2.9505	-1.00267
C31	-5.18482	3.377787	0.191122
C32	-4.46862	3.463169	1.360717
C33	-3.0835	3.186986	1.360382
C34	-2.41743	2.75247	0.226945
H35	-6.23504	3.653899	0.154879
H36	-4.94968	3.791647	2.277214
H37	-2.50814	3.356658	2.265576
C38	-1.9043	-0.4565	0.784847
C39	-2.64501	-1.40462	1.570774
C40	-2.54256	-1.40725	2.983647
C41	-1.7385	-0.49614	3.62052
C42	-1.02004	0.441559	2.855232
C43	-1.07465	0.489993	1.468596
H44	-3.11366	-2.14268	3.543503
H45	-1.6546	-0.48854	4.703104
H46	-0.3925	1.167179	3.36441
H47	-4.98919	2.622848	-4.36975
H48	-6.25666	3.262385	-2.29913
C49	-0.91631	2.681189	0.243601
C50	-0.2634	1.568452	0.816433
C51	1.141689	1.562329	0.945524
C52	1.881969	2.67933	0.512092
C53	1.232142	3.78703	-0.06831
C54	-0.17226	3.7982	-0.19645
C59	-1.38593	-0.55421	-3.90813
H60	-0.75936	0.047647	-4.54859
H61	-0.96661	-1.4186	-3.41981
H62	-2.42855	-0.32524	-3.79621
O63	-1.90208	-1.68895	-5.44976
C64	-3.00976	-2.26797	-5.18847
O65	-3.70414	-2.2208	-4.16621
C66	-3.51372	-3.18513	-6.3404
F67	-3.11026	-4.45763	-6.12071
F68	-4.85893	-3.18977	-6.40332
F69	-3.05016	-2.81262	-7.54641
C69	2.063365	4.951405	-0.57317
H70	1.465073	5.702133	-1.08576
H71	2.591751	5.455301	0.24562
H72	2.818796	4.603773	-1.28498

C72	3.389905	2.661584	0.657539
H73	3.823872	3.659627	0.600999
H74	3.697127	2.22407	1.611734
H75	3.851093	2.059467	-0.13611
C75	-0.86428	5.004616	-0.80284
H76	-0.60177	5.117319	-1.86012
H77	-1.94933	4.933037	-0.73745
H78	-0.56972	5.929692	-0.29608
C78	1.86822	0.362865	1.523488
H79	2.180611	0.532548	2.562437
H80	1.244516	-0.5315	1.514886
H81	2.776995	0.141164	0.958067

Table S453. $[\text{Rh}^{\text{III}}\text{-I}(\text{bisq}^{\text{Me4}})(\text{Me}_{\text{ax}}\cdots\text{TFA})(\text{TFA}_{\text{eq}})(\text{TFAH}_{\text{eq}})]^{\dagger}$
thermodynamic values

Temp	298.15	498.15
E_{gas}	-2918.86	-2918.86
E_{solv}	-2918.89	-2918.89
G	-2918.37	-2918.47
ZPE	364.136	364.136
H_{vib}	29.666	74.572
S_{trans}	46.083	48.634
S_{rot}	39.165	40.695
S_{vib}	196.513	309.881
solv	-18.7	-18.7

Table S454. $[\text{Rh}^{\text{III-I}}(\text{bisq}^{\text{Me4}})(\text{Me}_{\text{eq}}\cdots\text{TFA})(\text{TFA})_2]^{\dagger}$
Cartesian coordinates

Atom	x	y	z
Rh1	-1.24592	0.421688	-2.26283
N2	-1.91412	-1.34032	0.316563
C3	-2.37955	-2.55769	0.11988
C4	-3.03963	-3.31055	1.125859
C5	-3.18989	-2.76138	2.37505
C6	-6.0765	0.896246	-2.18811
C7	-5.45574	0.267412	-3.2408
C8	-4.04891	0.189692	-3.27838

N9	-3.27552	0.704318	-2.32366
H10	-2.20127	-2.97352	-0.86971
H11	-3.40626	-4.30744	0.898109
H12	-3.68435	-3.30639	3.176527
O13	-1.57845	-1.11735	-3.64629
H14	-3.52601	-0.33445	-4.07012
O15	0.744302	-0.04178	-1.95587
C16	1.517607	-0.66934	-2.7653
O17	1.430744	-0.88986	-3.9656
C18	2.80932	-1.15652	-2.04125
F19	3.360817	-2.21807	-2.65155
F20	3.753595	-0.16819	-2.04305
F21	2.612584	-1.49512	-0.74611
C22	-1.34637	-2.37376	-3.54764
O23	-0.94064	-3.05427	-2.61362
C24	-1.73813	-3.08346	-4.87709
F25	-1.48009	-4.40272	-4.84876
F26	-3.07853	-2.94737	-5.09897
F27	-1.10797	-2.56481	-5.94555
C28	-3.86741	1.352336	-1.25905
C29	-5.28611	1.465672	-1.15725
C30	-5.84161	2.14035	-0.04115
C31	-5.01707	2.690514	0.912862
C32	-3.61427	2.586301	0.79197
C33	-3.02248	1.919748	-0.26752
H34	-6.92265	2.216511	0.041858
H35	-5.44119	3.213953	1.765626
H36	-2.98106	3.039063	1.547335
C37	-2.03816	-0.78039	1.550778
C38	-2.67368	-1.46592	2.636219
C39	-2.7434	-0.85552	3.913352
C40	-2.18028	0.383342	4.111551
C41	-1.54372	1.055764	3.043786
C42	-1.46933	0.514578	1.77037
H43	-3.23239	-1.38612	4.727888
H44	-2.21796	0.852388	5.091597
H45	-1.09416	2.028277	3.225088
H46	-6.02468	-0.17767	-4.05067
H47	-7.16008	0.9683	-2.13275
C48	-1.52722	1.840782	-0.40158

C49	-0.77015	1.266534	0.679734
C50	0.606786	1.448637	0.737444
C51	1.253036	2.295468	-0.21087
C52	0.533399	2.913459	-1.22845
C53	-0.88006	2.701191	-1.34867
C58	-0.83486	1.504246	-4.44364
H59	-0.63976	0.527517	-4.85478
H60	-1.83172	1.911879	-4.4319
H61	-0.0281	2.06632	-4.0095
O62	-0.52192	2.328487	-6.22263
C63	-0.38082	3.59087	-6.16643
O64	-0.4274	4.36982	-5.20768
C65	-0.1561	4.246623	-7.56278
F66	0.2931	3.389029	-8.49855
F67	-1.32307	4.765918	-8.02326
F68	0.727857	5.265097	-7.49291
C68	2.750815	2.493576	-0.1139
H69	3.059522	3.469115	-0.49447
H70	3.110262	2.413161	0.914585
H71	3.271829	1.728624	-0.70253
C71	1.257034	3.811708	-2.21344
H72	0.650802	4.091009	-3.07458
H73	1.594811	4.741472	-1.73409
H74	2.151996	3.311888	-2.59944
C74	1.458331	0.690913	1.735944
H75	2.225103	0.120429	1.201875
H76	1.971794	1.355642	2.442591
H77	0.867893	-0.01612	2.31778
C77	-1.69338	3.701289	-2.15718
H78	-1.3119	3.862504	-3.16617
H79	-2.74031	3.413313	-2.23997
H80	-1.66739	4.673817	-1.64383

Table S455. $[\text{Rh}^{\text{III}}\text{-I}(\text{bisq}^{\text{Me4}})(\text{Me}_{\text{eq}}\cdots\text{TFA})(\text{TFA})_2]^{+}$ thermodynamic values

Temp	298.15	498.15
E_{gas}	-2918.35	-2918.35
E_{solv}	-2918.42	-2918.42
G	-2917.92	-2918.02

ZPE	355.959	355.959
H_{vib}	28.966	73.103
S_{trans}	46.080	48.630
S_{rot}	39.231	40.761
S_{vib}	200.622	314.088
solv	-46.7	-46.7

Table S456. [Rh^{III}-(bisq^{Me4})(Me_{eq}...TFAH)(TFA)₂][‡]
(TFAH H-bonded to TFA_{ax}) Cartesian coordinates

Atom	x	y	z
Rh1	-1.49153	0.566269	-1.93564
N2	-1.53772	-1.3947	-0.27375
C3	-1.73179	-2.66479	-0.57217
C4	-2.46147	-3.55154	0.257618
C5	-2.99227	-3.07753	1.433256
C6	-6.217	1.248776	-1.08031
C7	-5.79214	0.190966	-1.84872
C8	-4.41305	0.004063	-2.07047
N9	-3.48893	0.819538	-1.56893
H10	-1.29584	-2.9996	-1.507
H11	-2.59177	-4.58548	-0.04627
H12	-3.56444	-3.7258	2.092636
O13	-2.05617	-0.8304	-3.68405
H14	-4.03991	-0.81649	-2.67212
O15	0.53004	0.399928	-2.36669
C16	1.078566	-0.73764	-2.59988
O17	0.575285	-1.84962	-2.74351
C18	2.628189	-0.63833	-2.65102
F19	3.161179	-1.56348	-3.4577
F20	3.067278	0.571235	-3.05977
F21	3.134365	-0.84185	-1.40377
C22	-1.45084	-1.49906	-4.52397
O23	-0.66178	-1.10689	-5.46603
C24	-1.73357	-3.01603	-4.63446
F25	-0.62182	-3.73672	-4.76286
F26	-2.41248	-3.45369	-3.55873
F27	-2.51041	-3.22725	-5.7185
C28	-3.88027	1.875195	-0.7742
C29	-5.26012	2.12704	-0.51232

C30	-5.61372	3.235765	0.296942
C31	-4.63182	4.043899	0.822614
C32	-3.26843	3.772281	0.570319
C33	-2.87137	2.702545	-0.21532
H34	-6.66383	3.432639	0.491135
H35	-4.89895	4.893653	1.443832
H36	-2.50823	4.411508	1.010522
C37	-2.02701	-0.90895	0.904022
C38	-2.77897	-1.72368	1.80383
C39	-3.25756	-1.16211	3.014521
C40	-2.97899	0.149519	3.320604
C41	-2.21465	0.947549	2.436408
C42	-1.74215	0.449777	1.23559
H43	-3.83239	-1.78422	3.696092
H44	-3.33452	0.579716	4.252492
H45	-1.98494	1.971895	2.714326
H46	-6.49491	-0.50575	-2.29299
H47	-7.27392	1.421604	-0.89719
C48	-1.41203	2.384639	-0.41007
C49	-0.85719	1.295013	0.352812
C50	0.552464	1.212321	0.548281
C51	1.380852	2.186018	-0.01311
C52	0.841047	3.261678	-0.77261
C53	-0.53521	3.391297	-0.94426
C58	-1.47742	2.155183	-3.84496
H59	-0.41663	2.078509	-3.6714
H60	-2.01058	1.352777	-4.32285
H61	-2.04335	2.964719	-3.41793
O62	-1.20426	3.118106	-5.47542
C63	-0.57228	2.424127	-6.3286
O64	-0.26569	1.219681	-6.3086
C65	-0.06977	3.212202	-7.56924
F66	-0.59268	4.445285	-7.64386
F67	1.271934	3.331712	-7.50977
F68	-0.38073	2.557066	-8.70099
H69	-0.5491	-0.09469	-5.60883
C69	2.88169	2.111903	0.157184
H70	3.304895	3.085113	0.424297
H71	3.181676	1.397895	0.922308
H72	3.353926	1.798685	-0.7809

C72	1.803248	4.256437	-1.38715
H73	1.312054	4.957969	-2.05992
H74	2.31999	4.846499	-0.61947
H75	2.578171	3.738132	-1.9619
C75	1.155983	0.071478	1.343085
H76	1.83137	-0.51578	0.713024
H77	1.738301	0.438289	2.196126
H78	0.399033	-0.6049	1.734987
C78	-1.10111	4.592846	-1.67726
H79	-0.69876	4.673686	-2.69232
H80	-2.18721	4.550621	-1.75886
H81	-0.85022	5.527323	-1.16129

Table S457. $[\text{Rh}^{\text{III}}\text{-I}(\text{bisq}^{\text{Me4}})(\text{Me}_{\text{eq}}\cdots\text{TFAH})(\text{TFA})_2]^{\dagger}$
(TFAH H-bonded to TFA_{ax}) thermodynamic values

Temp	298.15	498.15
E_{gas}	-2918.84	-2918.84
E_{solv}	-2918.87	-2918.87
G	-2918.35	-2918.45
ZPE	363.955	363.955
H_{vib}	29.423	74.126
S_{trans}	46.083	48.634
S_{rot}	39.024	40.554
S_{vib}	199.564	313.443
solv	-16.3	-16.3

Table S458. $[\text{Rh}^{\text{III}}\text{-I}(\text{bisq}^{\text{Me4}})(\text{Me}_{\text{eq}}\cdots\text{TFAH})(\text{TFA})_2]^{\dagger}$
(TFAH H-bonded to TFA_{eq}) Cartesian coordinates

Atom	x	y	z
Rh1	-1.41041	0.58378	-1.64227
N2	-1.68072	-1.36951	0.075884
C3	-2.02186	-2.60617	-0.22628
C4	-2.71798	-3.45905	0.665917
C5	-3.05739	-2.98044	1.908478
C6	-6.21019	1.154364	-1.31526
C7	-5.66715	0.253493	-2.19963
C8	-4.26702	0.124033	-2.29475

N9	-3.42739	0.855961	-1.56388
H10	-1.7511	-2.94535	-1.22407
H11	-2.96886	-4.47023	0.360772
H12	-3.58739	-3.60356	2.624379
O13	-1.74783	-0.92924	-3.07137
H14	-3.80207	-0.59035	-2.96467
O15	0.667252	0.010332	-1.79149
C16	1.456283	0.445769	-2.63483
O17	1.467106	1.648348	-3.09191
C18	2.653296	-0.45071	-3.01843
F19	3.086748	-0.18335	-4.25507
F20	3.664555	-0.18053	-2.15114
F21	2.367681	-1.74993	-2.92376
C22	-1.0015	-1.28187	-4.05211
O23	-0.01111	-0.7358	-4.53675
C24	-1.50838	-2.61224	-4.67292
F25	-0.8103	-2.97014	-5.75429
F26	-1.42161	-3.62014	-3.77028
F27	-2.80967	-2.50712	-5.03225
C28	-3.94027	1.776881	-0.67308
C29	-5.34859	1.94836	-0.51728
C30	-5.82376	2.904722	0.414739
C31	-4.93461	3.658488	1.146331
C32	-3.54355	3.488131	0.972265
C33	-3.03109	2.561899	0.079481
H34	-6.89608	3.032272	0.535175
H35	-5.29804	4.391827	1.860213
H36	-2.85508	4.098817	1.549789
C37	-2.01775	-0.86612	1.296873
C38	-2.71296	-1.65144	2.269146
C39	-3.02111	-1.08832	3.532825
C40	-2.65047	0.20533	3.816674
C41	-1.96857	0.981915	2.851513
C42	-1.65329	0.4806	1.600686
H43	-3.54578	-1.6931	4.268478
H44	-2.87713	0.639624	4.786234
H45	-1.67763	1.998392	3.101227
H46	-6.2923	-0.37054	-2.82939
H47	-7.28612	1.270514	-1.21761
C48	-1.54583	2.394796	-0.08937

C49	-0.88188	1.36116	0.646529
C50	0.538073	1.413405	0.79261
C51	1.253003	2.488563	0.263259
C52	0.592238	3.532514	-0.44669
C53	-0.78974	3.488272	-0.6313
C58	-1.23854	2.146664	-3.78344
H59	-0.88527	1.203293	-4.16424
H60	-2.29423	2.372408	-3.82375
H61	-0.60249	2.724441	-3.14057
O62	-0.84747	3.082717	-5.35301
C63	0.312942	2.95923	-5.84255
O64	1.337161	2.400162	-5.39145
C65	0.501979	3.665531	-7.21258
F66	-0.65391	3.775361	-7.88211
F67	0.983884	4.909315	-7.00094
F68	1.375654	3.004611	-7.98267
H69	1.472455	1.884051	-4.15857
C69	2.759398	2.503324	0.419787
H70	3.196366	3.478998	0.211005
H71	3.062062	2.214902	1.430891
H72	3.225046	1.784263	-0.2672
C72	1.414273	4.670469	-1.01682
H73	0.799796	5.424479	-1.50677
H74	1.987736	5.182536	-0.23594
H75	2.133001	4.299757	-1.75673
C75	1.27441	0.302259	1.508227
H76	2.068191	-0.10116	0.870471
H77	1.748486	0.656187	2.432515
H78	0.614184	-0.52339	1.769782
C78	-1.51609	4.590586	-1.38084
H79	-1.03708	4.816969	-2.33794
H80	-2.5498	4.31803	-1.59428
H81	-1.53752	5.524835	-0.80588

Table S459. [Rh^{III}](bisq^{Me4})(Me_{eq}...TFAH)(TFA)₂)[†]
(TFAH H-bonded to TFA_{eq}) thermodynamic values

Temp	298.15	498.15
E _{gas}	-2918.84	-2918.84

E _{solv}	-2918.86	-2918.86
G	-2918.34	-2918.44
ZPE	362.671	362.671
H _{vib}	29.370	74.071
S _{trans}	46.083	48.634
S _{rot}	39.050	40.580
S _{vib}	199.030	312.893
solv	-13.3	-13.3

Table S460. [Rh^{III}]
[(bisq^{Me4})(Me_{eq}...TFA)(TFA_{ax})(TFAH_{eq})][†] Cartesian coordinates

Atom	x	y	z
Rh1	-1.27503	0.38908	-2.08928
N2	-2.00523	-1.20636	0.065035
C3	-2.60196	-2.33592	-0.27004
C4	-3.23425	-3.19978	0.655462
C5	-3.23928	-2.8509	1.982559
C6	-6.03892	1.22626	-1.90471
C7	-5.49912	0.570125	-2.98477
C8	-4.10389	0.384294	-3.05809
N9	-3.27048	0.828212	-2.12217
H10	-2.59344	-2.58305	-1.32732
H11	-3.70052	-4.11541	0.305447
H12	-3.71317	-3.48205	2.730109
O13	-1.86987	-1.39191	-3.12418
H14	-3.6621	-0.16729	-3.87572
O15	0.810604	-0.10877	-1.90329
C16	1.713398	-0.63283	-2.56466
O17	1.679198	-1.21877	-3.70201
C18	3.14586	-0.56373	-1.98201
F19	3.929723	-1.53312	-2.45818
F20	3.698018	0.625802	-2.30459
F21	3.118251	-0.66289	-0.64249
H22	0.716485	-1.46106	-4.11095
C23	-1.46542	-2.08795	-4.09339
O24	-0.37369	-2.06431	-4.69682
C25	-2.52712	-3.10031	-4.59528
F26	-2.07811	-3.87392	-5.58261

F27	-2.92751	-3.89761	-3.58034
F28	-3.61545	-2.43109	-5.04173
C29	-3.77838	1.515855	-1.04109
C30	-5.18153	1.723409	-0.89224
C31	-5.65328	2.41327	0.252821
C32	-4.76184	2.886325	1.187777
C33	-3.37282	2.69691	1.01279
C34	-2.86554	2.018962	-0.08198
H35	-6.72267	2.561336	0.37422
H36	-5.12046	3.417051	2.064691
H37	-2.68475	3.094804	1.751708
C38	-1.99327	-0.83949	1.381677
C39	-2.61343	-1.64611	2.391237
C40	-2.58533	-1.23603	3.747583
C41	-1.95687	-0.06514	4.097219
C42	-1.33482	0.72643	3.107162
C43	-1.33238	0.372184	1.767288
H44	-3.06383	-1.86128	4.497348
H45	-1.93114	0.25668	5.134352
H46	-0.83571	1.644458	3.404746
H47	-6.1206	0.180535	-3.78347
H48	-7.11182	1.373732	-1.81551
C49	-1.3828	1.86768	-0.28086
C50	-0.62698	1.234333	0.771683
C51	0.740465	1.460385	0.879901
C52	1.386708	2.355785	-0.02861
C53	0.694451	2.915214	-1.09771
C54	-0.72351	2.716824	-1.22464
C59	-0.91893	1.367359	-4.24814
H60	-0.8722	0.400784	-4.72062
H61	-1.85173	1.902761	-4.20176
H62	-0.01598	1.856647	-3.92575
O63	-0.66026	2.101509	-6.09756
C64	-0.32777	3.331417	-6.06194
O65	-0.15263	4.07944	-5.09432
C66	-0.09879	3.963713	-7.46574
F67	-0.43655	3.149958	-8.48079
F68	-0.81971	5.097251	-7.59388
F69	1.203567	4.289115	-7.61722
C69	2.843259	2.70886	0.196325

H70	3.054393	3.735726	-0.10926
H71	3.122389	2.615968	1.247348
H72	3.511262	2.056483	-0.37701
C72	1.425566	3.802607	-2.08381
H73	0.908219	3.896911	-3.03923
H74	1.559201	4.81877	-1.68636
H75	2.424476	3.407594	-2.28889
C75	1.585011	0.742173	1.914915
H76	2.509927	0.375064	1.464698
H77	1.870244	1.40057	2.745565
H78	1.060075	-0.11171	2.341914
C78	-1.50118	3.726889	-2.05043
H79	-1.11787	3.838838	-3.06641
H80	-2.56226	3.490329	-2.1107
H81	-1.41619	4.710464	-1.56814

Table S461. [Rh^{III}-
'(bisq^{Me4})(Me_{eq}...TFA)(TFA_{ax})(TFAH_{eq})][‡]
thermodynamic values

Temp	298.15	498.15
E_{gas}	-2918.84	-2918.84
E_{solv}	-2918.87	-2918.87
G	-2918.36	-2918.45
ZPE	363.922	363.922
H_{vib}	29.824	74.812
S_{trans}	46.083	48.634
S_{rot}	39.205	40.735
S_{vib}	197.666	311.248
solv	-19.6	-19.6

Table S462. [Rh^{III}-
'(bisq^{Me4})(Me_{eq}...TFA)(TFA_{eq})(TFAH_{ax})][‡] Cartesian
coordinates

Atom	x	y	z
Rh1	-1.03999	1.037644	-1.76765
N2	-1.90333	-0.98996	-0.07813
C3	-2.46603	-2.03256	-0.66237
C4	-3.071	-3.10355	0.036645

C5	-3.08965	-3.06544	1.407791
C6	-5.81657	1.75896	-1.80975
C7	-5.16921	1.470146	-2.98727
C8	-3.76254	1.350622	-3.00296
N9	-3.03141	1.506136	-1.90338
H10	-2.44948	-2.03709	-1.7475
H11	-3.50688	-3.92928	-0.51682
H12	-3.54501	-3.86333	1.989705
O13	-1.63016	-0.58081	-3.23371
H14	-3.23317	1.122634	-3.92212
O15	0.965477	0.465697	-1.48781
C16	1.788651	-0.0805	-2.27017
O17	1.671719	-0.47639	-3.44669
C18	3.205134	-0.23958	-1.6537
F19	3.972625	-1.07877	-2.35329
F20	3.825557	0.966002	-1.62426
F21	3.14311	-0.69422	-0.38449
H22	0.564375	-0.83291	-4.23871
C23	-1.34775	-1.10705	-4.31549
O24	-0.1948	-1.21222	-4.86673
C25	-2.48242	-1.84273	-5.06064
F26	-2.18679	-2.10583	-6.3295
F27	-2.69057	-3.01958	-4.41561
F28	-3.62609	-1.1467	-5.00789
C29	-3.64431	1.850825	-0.72037
C30	-5.05945	1.973293	-0.62938
C31	-5.63292	2.308175	0.623171
C32	-4.82279	2.539533	1.711606
C33	-3.41712	2.450628	1.595219
C34	-2.81365	2.103356	0.399315
H35	-6.71363	2.384035	0.705271
H36	-5.26031	2.801903	2.670394
H37	-2.7989	2.658509	2.461928
C38	-1.90192	-0.93362	1.288779
C39	-2.50247	-1.966	2.082898
C40	-2.49717	-1.87621	3.49739
C41	-1.90898	-0.79933	4.115135
C42	-1.30226	0.212207	3.34004
C43	-1.27608	0.172724	1.954247
H44	-2.96238	-2.66978	4.076847

H45	-1.90227	-0.72162	5.198633
H46	-0.83244	1.051393	3.845552
H47	-5.71218	1.320047	-3.91386
H48	-6.89965	1.838646	-1.76983
C49	-1.31836	2.045159	0.247419
C50	-0.57422	1.248167	1.194306
C51	0.781776	1.477603	1.385532
C52	1.434664	2.539574	0.679322
C53	0.76024	3.275418	-0.28221
C54	-0.64695	3.065609	-0.51223
C59	-0.52407	2.270372	-3.71611
H60	-0.273	1.295955	-4.08896
H61	-1.53139	2.644116	-3.73405
H62	0.278961	2.927119	-3.41642
O63	-0.3989	2.852246	-5.62617
C64	-1.23162	2.152048	-6.29319
O65	-2.01448	1.273747	-5.90775
C66	-1.18889	2.460756	-7.81769
F67	-0.99711	3.770718	-8.06507
F68	-0.17455	1.780365	-8.39478
F69	-2.3286	2.091947	-8.4268
C69	1.627311	0.591602	2.277045
H70	1.911448	1.096722	3.209223
H71	1.108295	-0.32667	2.547441
H72	2.551418	0.314366	1.76462
C72	2.886395	2.834166	0.991346
H73	3.114665	2.65332	2.044248
H74	3.553304	2.19738	0.398869
H75	3.147007	3.871421	0.775405
C75	1.498774	4.343189	-1.0637
H76	0.942404	4.679784	-1.93806
H77	1.702243	5.231951	-0.45128
H78	2.464017	3.96745	-1.41576
C78	-1.42284	4.217067	-1.1368
H79	-1.11802	4.427581	-2.16333
H80	-2.49617	4.040505	-1.14458
H81	-1.24569	5.130405	-0.55526

Table S463. [Rh^{III}-'(bisq^{Me4})(Me_{eq}...TFA)(TFA_{eq})(TFAH_{ax})][‡]

thermodynamic values

Temp	298.15	498.15
E _{gas}	-2918.85	-2918.85
E _{solv}	-2918.87	-2918.87
G	-2918.35	-2918.45
ZPE	364.221	364.221
H _{vib}	29.803	74.793
S _{trans}	46.083	48.634
S _{rot}	39.061	40.591
S _{vib}	197.315	310.908
solv	-16.9	-16.9

Table S464. [Rh^{III-II}(bisq^{Me4})(Me_{ax}...OVCl₃)(TFA)₂][‡]

Cartesian coordinates

Atom	x	y	z
Rh1	-1.50758	0.23376	-1.92972
N2	-2.2549	-0.98705	-0.3466
C3	-3.04123	-2.02472	-0.61168
C4	-3.51919	-2.91984	0.362431
C5	-3.16331	-2.71584	1.670674
C6	-6.227	1.37149	-1.80517
C7	-5.68223	0.896231	-2.97367
C8	-4.28309	0.742654	-3.06534
N9	-3.46	1.059806	-2.07076
H10	-3.31566	-2.18994	-1.64376
H11	-4.14016	-3.75092	0.047982
H12	-3.4943	-3.38899	2.456894
H13	-3.81729	0.362716	-3.96832
O14	0.317486	-0.69032	-1.64864
C15	1.172868	-0.9203	-2.59306
O16	1.095233	-0.75006	-3.79883
C17	2.505246	-1.4987	-2.03661
F18	3.053128	-2.36426	-2.89764
F19	3.397318	-0.48702	-1.8496
F20	2.361547	-2.12678	-0.85311
O21	-0.69479	1.527888	-3.28379

C22	-1.09183	1.604708	-4.50395
O23	-1.97933	0.984581	-5.07934
C24	-0.33122	2.716723	-5.27357
F25	-0.42975	2.562173	-6.59643
F26	-0.87592	3.926359	-4.95785
F27	0.97424	2.773923	-4.95116
C28	-3.96373	1.669905	-0.9426
C29	-5.37409	1.789706	-0.75192
C30	-5.86471	2.339498	0.460397
C31	-4.98524	2.793806	1.415246
C32	-3.59214	2.757696	1.176276
C33	-3.06368	2.218418	0.016643
H34	-6.93857	2.407446	0.6102
H35	-5.35618	3.217311	2.343767
H36	-2.9162	3.191673	1.907147
C37	-1.91582	-0.72284	0.967207
C38	-2.35853	-1.60152	2.010394
C39	-1.99884	-1.34309	3.355768
C40	-1.24268	-0.24048	3.668259
C41	-0.82878	0.635409	2.645121
C42	-1.14165	0.426713	1.309627
H43	-2.33642	-2.02992	4.126204
H44	-0.96555	-0.03385	4.697456
H45	-0.24288	1.511151	2.905397
H46	-6.29675	0.599625	-3.8162
H47	-7.30361	1.453073	-1.68047
C48	-1.59349	2.340292	-0.28198
C49	-0.66141	1.444751	0.320205
C50	0.731082	1.665307	0.174403
C51	1.175716	2.751041	-0.59272
C52	0.251047	3.631686	-1.20705
C53	-1.13132	3.447354	-1.03392
C58	-1.74481	-1.59459	-3.49984
H59	-1.04835	-1.15347	-4.19722
H60	-1.38903	-2.31749	-2.78192
H61	-2.79662	-1.3665	-3.56889
C61	0.772152	4.745856	-2.08985
H62	-0.02613	5.307387	-2.56974
H63	1.387177	5.456007	-1.52447
H64	1.393826	4.333491	-2.8904

C64	2.665116	2.940574	-0.78601
H65	2.914377	3.910849	-1.21265
H66	3.205799	2.844542	0.16066
H67	3.062304	2.170691	-1.45941
C67	-2.11066	4.399068	-1.68975
H68	-2.06476	4.300941	-2.77949
H69	-3.13839	4.213066	-1.37934
H70	-1.88166	5.441109	-1.44492
C70	1.738111	0.730063	0.808295
H71	2.562937	0.525284	0.126322
H72	2.17116	1.165687	1.719315
H73	1.294224	-0.22866	1.070737
O74	-2.0287	-3.15687	-4.7971
V75	-3.49288	-3.80265	-5.08014
Cl76	-4.30871	-4.44743	-3.12016
Cl77	-4.82281	-2.19976	-5.79559
Cl78	-3.46919	-5.46776	-6.46834

Table S465. $[\text{Rh}^{\text{III-II}}(\text{bisq}^{\text{Me4}})(\text{Me}_{\text{ax}}\cdots\text{OVCl}_3)(\text{TFA})_2]^{\ddagger}$
thermodynamic values

Temp	298.15	498.15
E_{gas}	-3919.42	-3919.42
E_{solv}	-3919.45	-3919.45
G	-3918.97	-3919.06
ZPE	344.781	344.781
H_{vib}	30.344	74.892
S_{trans}	46.281	48.831
S_{rot}	39.341	40.871
S_{vib}	202.065	314.644
solv	-18.1	-18.1

Table S466. $[\text{Rh}^{\text{III-}}(\text{bisq}^{\text{Me4}})(\text{Me}_{\text{ax}}\cdots\text{OVCl}_3)(\text{TFA}_{\text{eq}})(\text{TFAH}_{\text{eq}})]^{+\ddagger}$
Cartesian coordinates

Atom	x	y	z
Rh1	-0.91317	0.432239	-1.62661
N2	-1.65049	-0.96176	-0.28709
C3	-1.86755	-2.22763	-0.62771

C4	-2.65196	-3.10129	0.147777
C5	-3.24645	-2.62081	1.291618
C6	-5.39227	2.414442	-1.81069
C7	-5.08315	1.231895	-2.4357
C8	-3.77759	0.731687	-2.31107
N9	-2.80949	1.339693	-1.62734
H10	-1.42056	-2.56985	-1.55291
H11	-2.79892	-4.12049	-0.19081
H12	-3.90202	-3.25041	1.886048
H13	-3.52618	-0.20307	-2.79201
O14	0.797371	-0.77319	-1.58528
C15	2.035226	-0.55955	-1.72175
O16	2.628708	0.449878	-2.15038
C17	2.931892	-1.76214	-1.32493
F18	3.164222	-2.51924	-2.40895
F19	4.100038	-1.34138	-0.82815
F20	2.331278	-2.52927	-0.39591
O21	-0.46603	1.91896	-3.09439
C22	0.503129	2.510988	-3.59812
O23	1.74989	2.317195	-3.42652
C24	0.175227	3.628318	-4.61839
F25	-1.01468	4.17792	-4.3399
F26	1.107937	4.584783	-4.59994
F27	0.124471	3.087241	-5.8448
H28	2.03758	1.473073	-2.80524
C29	-3.08832	2.520425	-0.9634
C30	-4.40522	3.084825	-1.05095
C31	-4.70635	4.294399	-0.37618
C32	-3.74426	4.92401	0.373758
C33	-2.45491	4.362681	0.466809
C34	-2.09865	3.187626	-0.17971
H35	-5.7079	4.704849	-0.46378
H36	-3.96754	5.847537	0.8983
H37	-1.70605	4.864829	1.071965
C38	-2.10575	-0.49372	0.926993
C39	-2.97945	-1.29722	1.721004
C40	-3.51245	-0.75628	2.919272
C41	-3.15015	0.506308	3.326679
C42	-2.20195	1.248497	2.585851
C43	-1.6607	0.769779	1.405104

H44	-4.19164	-1.36148	3.512486
H45	-3.55361	0.92189	4.244666
H46	-1.85567	2.201887	2.973604
H47	-5.8079	0.678791	-3.02193
H48	-6.38724	2.844455	-1.88246
C49	-0.70408	2.682316	0.023397
C50	-0.49917	1.482824	0.763843
C51	0.819621	1.088047	1.131756
C52	1.908891	1.879932	0.737011
C53	1.695099	3.094394	0.03731
C54	0.399493	3.485514	-0.34772
C59	-1.21464	-0.8152	-3.74049
H60	-1.59317	0.078031	-4.21519
H61	-0.15947	-1.03681	-3.77719
H62	-1.86917	-1.46683	-3.18461
C62	2.877372	3.970277	-0.31386
H63	2.601772	5.024545	-0.36794
H64	3.68088	3.878215	0.418138
H65	3.293798	3.691387	-1.29117
C65	3.325653	1.445874	1.054699
H66	3.999098	1.665818	0.223833
H67	3.71606	1.961897	1.941607
H68	3.397331	0.374822	1.241836
C68	0.207765	4.744677	-1.17211
H69	0.980836	4.835575	-1.93957
H70	-0.75983	4.760071	-1.67352
H71	0.273702	5.651259	-0.55783
C71	1.05482	-0.15663	1.963381
H72	1.796186	0.025513	2.745626
H73	0.145062	-0.49941	2.454445
H74	1.426415	-0.98412	1.348408
O75	-1.53148	-1.89835	-5.33529
V76	-3.03801	-2.35416	-5.77388
Cl77	-3.9401	-3.14625	-3.94224
Cl78	-4.08313	-0.53264	-6.32315
Cl79	-3.0164	-3.8214	-7.32958

Table S467. $[\text{Rh}^{\text{III}}\text{-II}(\text{bisq}^{\text{Me4}})(\text{Me}_{\text{ax}}\cdots\text{OVCl}_3)(\text{TFA}_{\text{eq}})(\text{TFAH}_{\text{eq}})]^{+\dagger}$
thermodynamic values

Temp	298.15	498.15
E _{gas}	-3919.82	-3919.82
E _{solv}	-3919.88	-3919.88
G	-3919.38	-3919.48
ZPE	351.778	351.778
H _{vib}	29.780	74.020
S _{trans}	46.284	48.834
S _{rot}	39.374	40.904
S _{vib}	201.677	314.453
solv	-36.4	-36.4

Table S468. $[\text{Rh}^{\text{III}}\text{-II}(\text{bisq}^{\text{Me4}})(\text{Me}_{\text{eq}}\cdots\text{OVCl}_3)(\text{TFA})_2]^\dagger$
Cartesian coordinates

Atom	x	y	z
Rh1	-1.29043	0.263426	-1.87341
N2	-1.84592	-1.10786	-0.22019
C3	-2.25835	-2.34244	-0.46049
C4	-2.75556	-3.18824	0.555856
C5	-2.8264	-2.71618	1.842473
C6	-6.05012	1.530086	-1.57722
C7	-5.57583	0.706089	-2.56568
C8	-4.1895	0.473967	-2.65863
N9	-3.29755	1.035759	-1.84693
H10	-2.16083	-2.69112	-1.48327
H11	-3.07401	-4.19212	0.296777
H12	-3.21882	-3.333	2.646337
O13	-1.87114	-0.76729	-3.54137
H14	-3.78813	-0.20147	-3.40415
O15	0.572486	-0.58412	-1.79079
C16	1.264544	-0.98205	-2.8104
O17	1.103395	-0.79279	-4.004
C18	2.49817	-1.80206	-2.33626
F19	3.148596	-2.35792	-3.35949
F20	3.381297	-0.98794	-1.68543
F21	2.153004	-2.77519	-1.4732
C22	-1.61229	-1.98795	-3.89501
O23	-1.12416	-2.90526	-3.25838
C24	-2.12815	-2.22035	-5.34284
F25	-1.84625	-3.45317	-5.77273

F26	-3.48296	-2.07778	-5.35236
F27	-1.61704	-1.3351	-6.20698
C28	-3.73453	1.935341	-0.89368
C29	-5.13429	2.176801	-0.71186
C30	-5.56916	3.068971	0.2992
C31	-4.65201	3.727389	1.082567
C32	-3.27319	3.531437	0.86128
C33	-2.79768	2.659637	-0.1049
H34	-6.63568	3.229958	0.429126
H35	-4.98006	4.415173	1.855881
H36	-2.55522	4.093043	1.451867
C37	-1.84009	-0.62392	1.063552
C38	-2.35935	-1.41064	2.1391
C39	-2.36696	-0.87914	3.452162
C40	-1.85306	0.373603	3.691766
C41	-1.29984	1.125428	2.632901
C42	-1.27906	0.655511	1.330158
H43	-2.77114	-1.4823	4.260619
H44	-1.85044	0.783273	4.697361
H45	-0.85669	2.094351	2.84548
H46	-6.23771	0.21083	-3.26749
H47	-7.11471	1.709514	-1.45331
C48	-1.3187	2.563868	-0.32669
C49	-0.59547	1.493365	0.279158
C50	0.827398	1.487282	0.216728
C51	1.494382	2.511674	-0.47511
C52	0.770232	3.604275	-1.01142
C53	-0.6388	3.629705	-0.95408
C54	-0.59467	1.737496	-3.62089
H55	-0.25116	0.915139	-4.23462
H56	-1.57052	2.176054	-3.77758
H57	0.066334	2.168538	-2.88703
C58	2.999109	2.42179	-0.62328
H59	3.378608	3.087231	-1.39755
H60	3.515507	2.6715	0.313222
H61	3.296729	1.406109	-0.8949
C62	1.504033	4.742396	-1.68865
H63	0.921836	5.664304	-1.67849
H64	2.460893	4.952552	-1.20719
H65	1.705635	4.500735	-2.74044

C66	-1.40269	4.765211	-1.60531
H67	-1.09271	4.90661	-2.64475
H68	-2.477	4.584376	-1.61193
H69	-1.23496	5.716155	-1.0847
C70	1.628992	0.414711	0.912685
H71	2.183564	-0.18077	0.184955
H72	2.356812	0.859651	1.601843
H73	0.998387	-0.26647	1.482555
O74	0.322475	3.116906	-4.86667
V75	-0.47162	3.705367	-6.16218
Cl76	0.726129	5.09904	-7.33016
Cl77	-1.13706	2.025343	-7.39359
Cl78	-2.26843	4.738126	-5.38575

Table S469. $[\text{Rh}^{\text{III-II}}(\text{bisq}^{\text{Me4}})(\text{Me}_{\text{eq}}\cdots\text{OVCl}_3)(\text{TFA})_2]^{\dagger}$
thermodynamic values

Temp	298.15	498.15
E_{gas}	-3919.41	-3919.41
E_{solv}	-3919.44	-3919.44
G	-3918.96	-3919.05
ZPE	344.002	344.002
H_{vib}	30.285	74.485
S_{trans}	46.281	48.831
S_{rot}	39.326	40.856
S_{vib}	207.308	320.017
solv	-18.0	-18.0

Table S470. $[\text{Rh}^{\text{III-}}(\text{bisq}^{\text{Me4}})(\text{Me}_{\text{eq}}\cdots\text{OVCl}_3)(\text{TFA}_{\text{ax}})(\text{TFAH}_{\text{eq}})]^{+\dagger}$
Cartesian coordinates

Atom	x	y	z
Rh1	-1.1935	0.428942	-1.94985
N2	-1.82341	-1.02135	-0.268
C3	-2.44943	-2.12374	-0.66036
C4	-3.00278	-3.06033	0.234871
C5	-2.91285	-2.8148	1.582718
C6	-5.8588	1.699121	-1.72488
C7	-5.39375	1.018211	-2.82512

C8	-4.02244	0.712881	-2.92111
N9	-3.14158	1.085871	-1.9959
H10	-2.52784	-2.27477	-1.73122
H11	-3.49231	-3.94594	-0.15528
H12	-3.33556	-3.50452	2.307647
O13	-1.81387	-1.03268	-3.34114
H14	-3.64414	0.127345	-3.74685
O15	0.840505	-0.24751	-1.75323
C16	1.738322	-0.83292	-2.37736
O17	1.774045	-1.23132	-3.59026
C18	3.039093	-1.13816	-1.59252
F19	3.878622	-1.89789	-2.28467
F20	3.654292	0.025065	-1.29137
F21	2.726205	-1.75969	-0.44495
H22	0.873908	-1.16504	-4.14327
C23	-1.37443	-1.48289	-4.44603
O24	-0.2512	-1.35191	-4.95804
C25	-2.45158	-2.28168	-5.22619
F26	-1.97222	-2.81722	-6.33978
F27	-2.94634	-3.25875	-4.44187
F28	-3.46933	-1.44902	-5.54527
C29	-3.56285	1.82697	-0.91151
C30	-4.94606	2.125838	-0.7288
C31	-5.34233	2.850035	0.423805
C32	-4.39877	3.276005	1.330233
C33	-3.02788	3.020318	1.105345
C34	-2.59378	2.309219	-3.5E-05
H35	-6.39584	3.069177	0.570347
H36	-4.69952	3.833947	2.211382
H37	-2.29496	3.410238	1.804973
C38	-1.69503	-0.75271	1.073716
C39	-2.25765	-1.64654	2.043734
C40	-2.14457	-1.35804	3.427242
C41	-1.48656	-0.22554	3.842551
C42	-0.90778	0.639411	2.890377
C43	-0.98906	0.404178	1.525623
H44	-2.58049	-2.04774	4.144214
H45	-1.39686	0.004773	4.899464
H46	-0.37303	1.519073	3.236425
H47	-6.05789	0.691119	-3.61714

H48	-6.91581	1.923995	-1.61228
C49	-1.11728	2.167774	-0.28432
C50	-0.31657	1.368688	0.601958
C51	1.06948	1.570293	0.687691
C52	1.664514	2.61063	-0.06794
C53	0.901678	3.398328	-0.95997
C54	-0.48984	3.222462	-1.03715
C55	-0.50194	1.775722	-3.88973
H56	-0.41293	0.898999	-4.51227
H57	-1.45219	2.27588	-3.78783
H58	0.352377	2.123198	-3.33089
C59	1.58622	4.479264	-1.77244
H60	1.010119	4.765301	-2.65242
H61	1.740291	5.38894	-1.17769
H62	2.569962	4.155486	-2.12053
C63	3.136993	2.911448	0.084843
H64	3.322625	3.988099	0.076359
H65	3.548487	2.510016	1.009601
H66	3.711781	2.478876	-0.74344
C67	-1.32326	4.219723	-1.80976
H68	-1.00204	4.317467	-2.85026
H69	-2.3833	3.973737	-1.81382
H70	-1.22031	5.215838	-1.36247
C71	1.94119	0.69436	1.566036
H72	2.860048	0.41619	1.049116
H73	2.232008	1.208523	2.490294
H74	1.432405	-0.22598	1.84863
O75	0.019919	2.925022	-5.38164
V76	-1.07306	3.319033	-6.53973
Cl77	-0.17611	4.423565	-8.14528
Cl78	-1.92394	1.440519	-7.23078
Cl79	-2.62571	4.478337	-5.5328

Table S471. [Rh^{III}-
^{II}(bisq^{Me4})(Me_{eq}...OVCl₃)(TFA_{ax})(TFAH_{eq})]⁺⁺
thermodynamic values

Temp	298.15	498.15
E _{gas}	-3919.80	-3919.80
E _{solv}	-3919.86	-3919.86

G	-3919.37	-3919.46
ZPE	352.090	352.090
H_{vib}	30.421	75.082
S_{trans}	46.284	48.834
S_{rot}	39.347	40.877
S_{vib}	203.055	315.899
solv	-36.2	-36.2

Table S472. [Rh^{III}-

II(bisq^{Me4})(Me_{eq}...OVCl₃)(TFA_{eq})(TFAH_{ax})]⁺⁺

Cartesian coordinates

Atom	x	y	z
Rh1	-1.54422	0.638864	-1.74991
N2	-1.76166	-1.07238	-0.17974
C3	-2.08068	-2.29373	-0.58279
C4	-2.58523	-3.28515	0.285348
C5	-2.80067	-2.96469	1.603934
C6	-6.26148	1.48171	-0.93618
C7	-5.87027	0.565273	-1.88261
C8	-4.49792	0.350252	-2.1081
N9	-3.54809	1.010108	-1.4486
H10	-1.97103	-2.49678	-1.64159
H11	-2.8137	-4.27004	-0.10718
H12	-3.21695	-3.69114	2.296056
O13	-2.12805	-0.82767	-3.13556
H14	-4.16164	-0.37595	-2.83536
O15	0.571337	0.351744	-1.96678
C16	1.409887	0.262915	-2.87714
O17	1.242469	0.114056	-4.1354
C18	2.903895	0.399259	-2.49248
F19	3.692115	-0.24185	-3.34834
F20	3.222136	1.709111	-2.49977
F21	3.117495	-0.08442	-1.25891
H22	0.26828	-0.123	-4.46563
C23	-1.80349	-1.13146	-4.32665
O24	-0.89356	-0.67886	-5.03701
C25	-2.70915	-2.24877	-4.90856
F26	-2.43483	-2.50728	-6.17949
F27	-2.53745	-3.37253	-4.18198

F28	-4.00613	-1.88304	-4.80733
C29	-3.90201	1.942457	-0.49285
C30	-5.27981	2.197876	-0.20934
C31	-5.61478	3.160785	0.77453
C32	-4.62303	3.841759	1.441344
C33	-3.26716	3.587592	1.143845
C34	-2.88797	2.653418	0.193011
H35	-6.66252	3.352278	0.984969
H36	-4.87655	4.5821	2.193521
H37	-2.49619	4.143638	1.670086
C38	-1.90855	-0.7406	1.143051
C39	-2.46999	-1.66955	2.075154
C40	-2.65972	-1.27908	3.42467
C41	-2.28476	-0.02279	3.839005
C42	-1.67941	0.870996	2.928471
C43	-1.47841	0.536279	1.600002
H44	-3.09397	-1.99024	4.121675
H45	-2.42637	0.280495	4.871601
H46	-1.33754	1.838302	3.2854
H47	-6.59067	-0.00091	-2.46227
H48	-7.31302	1.668577	-0.73718
C49	-1.41942	2.440516	-0.08307
C50	-0.71561	1.483874	0.721471
C51	0.686368	1.548144	0.848466
C52	1.380703	2.613666	0.241913
C53	0.695865	3.603904	-0.51385
C54	-0.69109	3.528453	-0.68072
C59	-1.5395	2.299546	-3.61718
H60	-1.59876	1.527734	-4.36948
H61	-2.44655	2.721242	-3.21715
H62	-0.57967	2.594533	-3.22048
C62	1.487143	4.760896	-1.08794
H63	0.850889	5.548565	-1.48748
H64	2.130243	5.213709	-0.32707
H65	2.138965	4.425152	-1.90291
C65	2.871139	2.749293	0.451281
H66	3.073768	3.381605	1.326982
H67	3.351834	1.78795	0.626322
H68	3.363762	3.213518	-0.40268
C68	-1.43706	4.631969	-1.40246

H69	-1.01466	4.836349	-2.38992
H70	-2.49298	4.397862	-1.53445
H71	-1.38593	5.56951	-0.83568
C71	1.448469	0.512306	1.647878
H72	2.042371	0.974405	2.443481
H73	0.787542	-0.21801	2.111829
H74	2.140996	-0.03179	0.9982
O75	-1.47995	3.751278	-4.92175
V76	-0.30667	3.91992	-6.05511
Cl77	-0.50046	2.235622	-7.3939
Cl78	-0.50845	5.799678	-7.07335
Cl79	1.57632	3.821118	-4.96273

Table S473. [Rh^{III}-
^{II}(bisq^{Me4})(Me_{eq}...OVCl₃)(TFA_{eq})(TFAH_{ax})]^{+‡}
thermodynamic values

Temp	298.15	498.15
E _{gas}	-3919.81	-3919.81
E _{solv}	-3919.86	-3919.86
G	-3919.37	-3919.46
ZPE	351.930	351.930
H _{vib}	29.897	74.185
S _{trans}	46.284	48.834
S _{rot}	39.334	40.864
S _{vib}	202.562	315.462
solv	-35.6	-35.6

Table S474.
[Rh^{III}(bisq^{Me4})(CH₂TFA_{ax}...H...TFA_{eq})(TFA_{eq})]^{+‡}
Cartesian coordinates

Atom	x	y	z
Rh1	-2.73572	0.35273	-1.47533
N2	-1.51985	-0.75744	-0.09009
C3	-1.71299	-2.0742	-0.0656
C4	-1.06248	-2.94766	0.82194
C5	-0.18734	-2.42332	1.738791
C11	-6.05862	-0.38792	2.030052
C12	-6.20204	-1.06152	0.840815

C13	-5.29056	-0.81453	-0.20435
N14	-4.30574	0.071642	-0.10892
H15	-2.42997	-2.47384	-0.76662
H16	-1.27743	-4.00799	0.76231
H17	0.331201	-3.05862	2.451234
H23	-5.36052	-1.38449	-1.11913
O28	-1.07591	0.793341	-2.65706
C29	-0.57587	-0.14968	-3.32551
O30	-1.005	-1.32913	-3.3752
C31	0.721699	0.182297	-4.09575
F32	0.900209	-0.63538	-5.12613
F33	0.699635	1.45046	-4.53682
F34	1.760615	0.053008	-3.24474
O35	-3.99679	1.415116	-2.70854
C36	-3.85681	1.375813	-4.00337
O37	-3.0617	0.742655	-4.67445
C38	-4.94669	2.236429	-4.7016
F39	-4.75034	2.294755	-6.01588
F40	-6.16401	1.709358	-4.46733
F41	-4.94872	3.504798	-4.22041
H42	-2.21464	-1.25066	-2.92825
C43	-3.56806	-1.46646	-2.92138
H44	-3.40376	-1.70122	-3.97834
H46	-4.45192	-0.8399	-2.87377
C41	0.046358	-1.02782	1.760287
C42	-0.63347	-0.1943	0.811561
C35	-0.36714	1.205411	0.812961
C44	0.52171	1.717461	1.748435
C45	1.172863	0.901526	2.694193
C46	0.943302	-0.45275	2.695265
H50	0.716927	2.785533	1.747598
H51	1.856395	1.347473	3.40948
H52	1.44527	-1.10485	3.403907
C47	-4.17789	0.814973	1.047742
C48	-5.03028	0.576607	2.167317
C49	-4.82651	1.320704	3.357084
C50	-3.83515	2.272763	3.416437
C51	-3.03852	2.542334	2.281195
C52	-3.20099	1.840451	1.098817
H55	-5.46945	1.130422	4.2113

H56	-3.6783	2.843405	4.326258
H57	-2.30129	3.338546	2.326358
H53	-6.72699	-0.5779	2.865035
H54	-6.98431	-1.79677	0.690389
C55	-1.00827	2.146023	-0.14282
C56	-2.45013	2.259769	-0.14385
C57	-3.06119	3.325367	-0.91916
C58	-2.26387	4.137077	-1.73224
C59	-0.8669	3.90362	-1.80835
C60	-0.23054	2.923504	-1.00124
O62	-3.8354	-2.67915	-2.1906
C63	-3.80401	-3.85584	-2.85819
O64	-3.61951	-4.0169	-4.03023
C65	-4.03592	-4.99402	-1.84068
F66	-3.01508	-5.00862	-0.94743
F67	-5.17598	-4.79095	-1.15827
F68	-4.08885	-6.16881	-2.4489
C68	-2.87732	5.26853	-2.53292
H69	-2.29334	6.187193	-2.43288
H70	-2.92454	5.01847	-3.59813
H71	-3.89268	5.496502	-2.21534
C71	-0.0133	4.67231	-2.78195
H72	-0.54977	5.468333	-3.29181
H73	0.863866	5.107263	-2.2917
H74	0.365839	3.983637	-3.54804
C74	1.260305	2.708431	-1.15674
H75	1.606734	1.823115	-0.62671
H76	1.521604	2.581	-2.21014
H77	1.835649	3.565461	-0.78642
C77	-4.53976	3.599038	-0.80357
H78	-4.99387	3.663383	-1.79305
H79	-5.06805	2.828584	-0.24711
H80	-4.70916	4.554187	-0.28991

Table S475.

$[\text{Rh}^{\text{III}}(\text{bisq}^{\text{Me4}})(\text{CH}_2\text{TFA}_{\text{ax}}\cdots\text{H}\cdots\text{TFA}_{\text{eq}})(\text{TFA}_{\text{eq}})]^{+\ddagger}$
thermodynamic values

Temp	298.15	498.15
E _{gas}	-2918.01	-2918.01

E _{solv}	-2918.08	-2918.08
G	-2917.57	-2917.66
ZPE	357.414	357.414
H _{vib}	28.731	73.181
S _{trans}	46.080	48.630
S _{rot}	38.838	40.368
S _{vib}	188.353	300.552
solv	-43.2	-43.2

Table S476.

$[\text{Rh}^{\text{III}}(\text{bisq}^{\text{Me4}})(\text{CH}_2\text{TFA}_{\text{eq}}\cdots\text{H}\cdots\text{TFA}_{\text{ax}})(\text{TFA}_{\text{eq}})]^{+\ddagger}$
Cartesian coordinates

Atom	x	y	z
Rh1	-1.38727	0.115241	-1.59387
N2	-1.9203	-1.26335	-0.1058
C3	-2.11078	-2.55255	-0.35561
C4	-2.65771	-3.42594	0.606469
C5	-3.03135	-2.92907	1.83411
C11	-6.16764	1.37018	-1.514
C12	-5.67311	0.303114	-2.21992
C13	-4.29172	0.053528	-2.18392
N14	-3.41796	0.80659	-1.51837
H15	-1.85269	-2.89792	-1.34886
H16	-2.79202	-4.47092	0.350753
H17	-3.48548	-3.57362	2.581464
H22	-3.88534	-0.79399	-2.71855
O27	0.435366	-0.82542	-1.64337
C28	1.497354	-0.31236	-2.18912
O29	1.662486	0.80078	-2.65864
C30	2.682646	-1.31848	-2.15411
F31	3.188353	-1.37069	-0.89288
F32	2.293889	-2.55814	-2.49109
F33	3.660014	-0.93726	-2.97383
H34	-0.13907	1.881785	-3.99035
H35	-0.71502	0.471449	-3.72827
O36	-1.91812	-1.37635	-2.9556
C37	-1.35718	-1.3922	-4.09194
O38	-0.64254	-0.48178	-4.56197
C39	-1.64785	-2.65046	-4.94086

F40	-0.94154	-2.65484	-6.0634
F41	-1.35557	-3.74535	-4.22285
F42	-2.95884	-2.66733	-5.23724
C43	-0.88165	1.719914	-3.1957
H45	-0.48119	2.317144	-2.38538
C41	-5.27999	2.195358	-0.78563
C42	-3.87523	1.904354	-0.81245
C35	-2.98437	2.773139	-0.11396
C44	-3.51502	3.839281	0.598957
C45	-4.89622	4.109054	0.645737
C46	-5.76547	3.303208	-0.04649
H50	-2.83393	4.489774	1.13916
H51	-5.26037	4.956	1.218232
H52	-6.83336	3.500186	-0.04577
C47	-2.1983	-0.75163	1.136774
C48	-2.80508	-1.56342	2.139257
C49	-3.12381	-0.97511	3.389577
C50	-2.81549	0.344847	3.629236
C51	-2.15018	1.115164	2.648249
C52	-1.83102	0.586364	1.409962
H55	-3.59949	-1.58365	4.152885
H56	-3.05379	0.795572	4.587455
H57	-1.85777	2.134604	2.882766
H53	-7.22976	1.597655	-1.50508
H54	-6.31362	-0.35292	-2.79829
C55	-1.5062	2.590001	-0.09846
C56	-0.97002	1.368222	0.442923
C57	0.459055	1.239017	0.606017
C58	1.301584	2.260617	0.150591
C59	0.747991	3.463008	-0.3508
C60	-0.65396	3.624735	-0.51072
O62	-2.16982	2.219048	-3.63262
C63	-2.18048	3.401792	-4.26045
O64	-1.23008	4.083829	-4.54151
C65	-3.64467	3.82224	-4.51371
F66	-4.35943	2.822278	-5.05321
F67	-4.21087	4.142869	-3.32298
F68	-3.70275	4.882566	-5.31042
C68	1.677597	4.584717	-0.73996
H69	2.529731	4.648723	-0.06005

H70	2.083347	4.410486	-1.74585
H71	1.180602	5.553819	-0.74958
C71	2.805352	2.104966	0.232883
H72	3.292873	2.560491	-0.63102
H73	3.212162	2.582839	1.133884
H74	3.105328	1.057838	0.249847
C74	1.052614	0.059036	1.337436
H75	1.630695	-0.57709	0.662829
H76	1.735901	0.40617	2.119624
H77	0.296943	-0.56469	1.810345
C77	-1.18071	4.881857	-1.18054
H78	-2.22462	4.780307	-1.47494
H79	-1.10783	5.756666	-0.52341
H80	-0.60848	5.108278	-2.08431

Table S477.

$[\text{Rh}^{\text{III}}(\text{bisq}^{\text{Me4}})(\text{CH}_2\text{TFA}_{\text{eq}}\cdots\text{H}\cdots\text{TFA}_{\text{ax}})(\text{TFA}_{\text{eq}})]^{+\ddagger}$
thermodynamic values

Temp	298.15	498.15
E_{gas}	-2918.02	-2918.02
E_{solv}	-2918.08	-2918.08
G	-2917.57	-2917.66
ZPE	357.803	357.803
H_{vib}	28.598	72.926
S_{trans}	46.080	48.630
S_{rot}	38.755	40.285
S_{vib}	187.560	299.444
solv	-41.8	-41.8

Table S478.

$[\text{Rh}^{\text{III}}(\text{bisq}^{\text{Me4}})(\text{CH}_2\text{TFA}_{\text{eq}}\cdots\text{H}\cdots\text{TFA}_{\text{eq}})(\text{TFA}_{\text{ax}})]^{+\ddagger}$
Cartesian coordinates

Atom	x	y	z
Rh1	-2.57787	0.117475	-1.33876
N2	-1.5005	-1.10102	-0.01273
C3	-1.68773	-2.41517	0.027467
C4	-1.01185	-3.2442	0.943203
C5	-0.13651	-2.68014	1.839911

C11	-5.75593	0.040408	2.382843
C12	-5.95944	-0.71877	1.256042
C13	-5.07839	-0.58013	0.167107
N14	-4.07074	0.289468	0.163501
H15	-2.39726	-2.82188	-0.68165
H16	-1.20255	-4.31127	0.923611
H17	0.390726	-3.2913	2.567017
H23	-5.16755	-1.21448	-0.70548
O28	-1.08242	-0.37404	-2.69121
C29	-1.14384	0.182549	-3.82703
O30	-1.93232	1.096401	-4.15206
C31	-0.10796	-0.27167	-4.88076
F32	0.827664	0.703333	-5.00153
F33	0.507446	-1.39604	-4.5121
F34	-0.68916	-0.44857	-6.06238
H35	-3.93487	2.333722	-3.29673
H36	-2.84707	1.156276	-3.18989
O37	-3.54013	-1.56357	-1.93
C38	-3.67578	-2.00145	-3.15717
O39	-3.31266	-1.51308	-4.20402
C40	-4.40548	-3.376	-3.10852
F41	-4.67651	-3.82643	-4.32581
F42	-3.61004	-4.27444	-2.47854
F43	-5.55345	-3.28893	-2.40612
C44	-4.05051	1.458751	-2.64087
H46	-4.39927	1.831262	-1.68662
C41	-3.89339	1.136508	1.239657
C42	-4.71144	0.997258	2.404635
C43	-4.47517	1.833564	3.524383
C36	-3.49162	2.793614	3.476874
C45	-2.73785	2.972583	2.297417
C46	-2.92393	2.1722	1.181821
H49	-5.09298	1.710311	4.408982
H50	-3.30874	3.436194	4.332111
H51	-2.00495	3.773028	2.252503
C48	-0.60121	-0.50099	0.838952
C49	0.0957	-1.28306	1.811675
C50	1.003703	-0.64291	2.691281
C51	1.220314	0.711893	2.595013
C52	0.552754	1.467377	1.607041

C53	-0.34887	0.889167	0.728182
H55	1.529079	-1.24159	3.429434
H56	1.918485	1.204653	3.264101
H57	0.764369	2.529593	1.520587
H53	-6.76318	-1.44334	1.190031
H54	-6.39219	-0.07084	3.256419
C55	-0.96107	1.747542	-0.35049
C56	-2.16171	2.473485	-0.07414
C57	-2.52221	3.596862	-0.86014
C58	-1.67056	4.002852	-1.90437
C59	-0.45767	3.30656	-2.16955
C60	-0.10104	2.189402	-1.40796
O62	-5.07291	0.606257	-3.15898
C63	-5.38288	0.757147	-4.46283
O64	-4.94583	1.594376	-5.20507
C65	-6.45827	-0.26476	-4.8927
F66	-7.65052	0.353676	-4.93136
F67	-6.17574	-0.73803	-6.10387
F68	-6.55002	-1.29574	-4.03154
C68	-2.02553	5.199076	-2.75968
H69	-1.30663	6.013254	-2.6096
H70	-1.99673	4.942172	-3.82357
H71	-3.01484	5.596486	-2.54255
C71	0.470175	3.768379	-3.27295
H72	0.257414	4.783042	-3.60507
H73	1.5146	3.741553	-2.95049
H74	0.38598	3.110018	-4.14582
C74	-3.79975	4.363896	-0.57044
H75	-4.44427	4.419964	-1.45376
H76	-4.38074	3.905964	0.229376
H77	-3.58601	5.394976	-0.26764
C77	1.210899	1.483123	-1.66204
H78	1.240781	0.497689	-1.19908
H79	1.395776	1.356627	-2.73011
H80	2.050227	2.065647	-1.26083

Table S479.

$[\text{Rh}^{\text{III}}(\text{bisq}^{\text{Me4}})(\text{CH}_2\text{TFA}_{\text{eq}}\cdots\text{H}\cdots\text{TFA}_{\text{eq}})(\text{TFA}_{\text{ax}})]^{+\ddagger}$
thermodynamic values

Temp	298.15	498.15
E _{gas}	-2918.01	-2918.01
E _{solv}	-2918.08	-2918.08
G	-2917.57	-2917.66
ZPE	357.859	357.859
H _{vib}	28.494	72.831
S _{trans}	46.080	48.630
S _{rot}	38.747	40.277
S _{vib}	186.194	298.103
solv	-42.6	-42.6

Miscellanea

Table S480. CH₄ (g) Cartesian coordinates

Atom	X	y	z
C1	-1.2E-09	-7.6E-09	-2E-09
H2	0.629885	0.629885	0.629885
H3	-0.62989	-0.62989	0.629885
H4	0.629885	-0.62989	-0.62989
H5	-0.62989	0.629885	-0.62989

Table S481. CH₄ (g) thermodynamic values

Temp	298.15	498.15
E _{gas}	-40.49	-40.49
G	-40.46	-40.48
ZPE	27.932	27.932
H _{tot}	2.393	4.310
S _{tot}	44.474	49.340

Table S482. TFAH (ℓ) Cartesian coordinates

Atom	x	y	z
O1	0	0	0
C2	0	0	1.194706
O3	1.072154	0	1.992513
H4	1.866377	-0.00396	1.435555
C5	-1.29506	-0.01221	2.05074
F6	-1.30318	1.011869	2.920835

F7	-2.36925	0.086168	1.269449
F8	-1.37798	-1.15922	2.749115

Table S483. TFAH (ℓ) thermodynamic values

Temp	298.15	498.15
E _{gas}	-526.75	-526.75
G	-526.75	-526.77
ZPE	24.26	24.26
H _{tot}	4.512	9.917
S _{tot}	80.206	93.916
ΔG _{gas→liq}	-1.138	3.390

Table S484. CH₃TFA (g) Cartesian coordinates

Atom	x	y	z
O1	0	0	0
C2	0	0	1.197715
O3	1.055591	0	2.002014
C4	2.350226	0.004918	1.354793
C5	-1.30003	0.01049	2.046631
F6	-1.38678	1.150426	2.758643
F7	-2.37212	-0.0751	1.258934
F8	-1.3229	-1.02243	2.908143
H9	2.446987	-0.86788	0.709143
H10	2.466739	0.914613	0.765466
H11	3.073293	-0.02819	2.16504

Table S485. CH₃TFA (g) thermodynamic values

Temp	298.15	498.15
E _{gas}	-566.03	-566.03
G	-566.00	-566.03
ZPE	41.70	41.70
H _{tot}	5.582	12.258
S _{tot}	88.845	105.760

Table S486. OVCl₃ Cartesian coordinates

Atom	x	y	z
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V1	0	0	0
O2	0	0	1.553381
Cl3	2.036796	0	-0.67365
Cl4	-1.01827	1.763696	-0.67383
Cl5	-1.0192	-1.76316	-0.67382

Table S487. OVCl_3 thermodynamic values

Temp	298.15	498.15
E_{gas}	-1527.33	-1527.33
E_{solv}	-1527.34	-1527.34
G	-1527.34	-1527.36
ZPE	4.978	4.978
H_{vib}	2.320	5.264
S_{trans}	41.332	43.882
S_{rot}	26.729	28.259
S_{vib}	14.077	21.583
solv	-0.8	-0.8

Table S488. MeOVCl_3 Cartesian coordinates

Atom	x	y	z
V1	0	0	0
O2	0	0	1.720611
Cl3	2.091485	0	-0.60189
Cl4	-1.08005	1.602679	-0.96133
Cl5	-0.79518	-1.94064	-0.58372
C6	0.540306	-0.78871	2.777224
H7	1.628619	-0.83012	2.686303
H8	0.124152	-1.79809	2.728926
H9	0.261708	-0.31369	3.719785

Table S489. MeOVCl_3 thermodynamic values

Temp	298.15	498.15
E_{gas}	-1567.21	-1567.21
E_{solv}	-1567.21	-1567.21
G	-1567.18	-1567.21
ZPE	28.766	28.766
H_{vib}	4.057	8.882

S_{trans}	41.582	44.132
S_{rot}	29.793	31.324
S_{vib}	27.567	39.833
solv	-3.2	-3.2

Table S490. Redox free energies

	H⁺/TFAH	e⁻/TFAH
G	-260	-127.063